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CELLULOSE PRODUCTS

AND ARTIFICIAL RUBBER

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CELLULOSE, CELLULOSE PRODUCTS, AND RUBBER SUBSTITUTES.

CELLULOSE, CELLULOSE PRODUCTS, AND ARTIFICIAL RUBBER,

COMPRISING

THE PREPARATION OF CELLULOSE FROM WOOD AND STRAW; MANUFACTURE OF PARCHMENT; METHODS OF OBTAINING SUGAR AND ALCOHOL, AND OXALIC ACID; PRODUCTION OF VISCOSE AND VISCOID, NITRO-CELLULOSES, AND CELLULOSE ESTERS, ARTIFICIAL SILK, CELLULOID, RUBBER SUBSTITUTES, OIL-RUBBER, AND FACTIS.

BY

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AUTHORIZED TRANSLATION FROM THE GERMAN,

BY

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EDITOR OF "THE TECHNO-CHEMICAL RECEIPT BOOK."

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PREFACE.

Among the raw materials which nature has placed at our disposal for industrial purposes, Cellulose has from time immemorial occupied a prominent position, having from prehistoric days, continuously served for the production of tissues, and been, even for thousands of years, employed as a basis for the execution of writings. By the development of the science of chemistry, we have become acquainted with a large number of compounds, which have to be considered as derivatives of Cellulose, and we have learned of processes for the separation of this important body, in a pure form, from wood and straw.

The nitro-compounds, which can be prepared from Cellulose, form the starting point for all the explosive bodies in use at the present time; and the nitro-celluloses themselves have led to the invention of processes for the production of so-called artificial silk and of celluloid. The discovery of the peculiar compound, to which the term viscose has been applied, was the initiatory step towards the preparation of a series of bodies of technical importance—solutions of cellulose having created the basis for the preparation of lustra-cellulose, etc. The branches of industry thereby called into existence have in a comparatively short time developed into noteworthy manufactures, and scarcely a month passes by, without our becoming acquainted with new applications of the compounds derived from Cellulose.

It would appear that the problem of the production of fermentable sugar, and thence of that of alcohol, ether, acetic acid, etc., from Cellulose or wood, has at present more closely approached its final solution than it had, even a few years since; and by the perfection of methods for this purpose a radical revolution in certain industries may eventually be looked for.

In consideration of the far-reaching importance to the industries of Cellulose and the products capable of being prepared

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from the latter, the author has endeavored to bring together in a comprehensive manner everything that has up to the present time become known on this subject, and it is hoped, that he has produced a work which gives clear explanations of all questions pertaining to Cellulose and the products obtainable from it, and which will serve as a hand-book for all who may be professionally interested—from the forester to the manufacturer of artificial silk, lustra-cellulose and celluloid.

By reason of their extensive use for insulating purposes for electric lines, etc., substances which are available as substitutes for rubber have acquired great industrial importance, and a comprehensive description of their preparation is also here given, and it is believed may serve to arouse the interest of a large body of manufacturers.

Dr. J. Bersch.

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CELLULOSE, CELLULOSE PRODUCTS, AND RUBBER SUBSTITUTES.

I.

CELLULOSE.

The substance to which the term *cellulose* has been applied is very widely distributed throughout nature, it forming the structural basis of all vegetable organisms. All plants, from the unicellular bacterium up to the mammoth conifers of California, are built up of cells, the envelopes or walls of which consist, in every case, of one and the same body, namely, cellulose. In the higher plants the individual contiguous cells coalesce in such a way that, in certain places, their walls are broken up, tubular structures—the so-called vessels—which frequently attain extraordinary lengths, being thereby formed. There are vessels which extend from the roots to the tops of gigantic trees, and, as above stated, have been formed by the coalescence of individual cells of a more or less globular form.

While in many plants the cells, as well as the vessels formed from them, always remain soft, in others combinations are deposited in them by which the cellulose is changed in a characteristic manner, the walls of the vessels frequently acquiring considerable firmness; and the cellulose vessels are changed to wood-vessels. In herbaceous plants such a transformation does not take place, and hence they have to be sharply distinguished from the

wood-forming plants, and the process of the formation of wood will have to be more closely discussed.

OCCURRENCE OF CELLULOSE.

While formerly the opinion prevailed that cellulose occurs exclusively in the vegetable organism, more recent investigations have also shown its presence, though to a limited extent, in the animal kingdom, its occurrence in many Tunicata having been definitely established, and it has also been found in insects and other articulates. Its occurrence in the skins of snakes has not been finally proved. It is also claimed that cellulose is formed in the human organism during certain morbid processes (tuberculosis). However, such occurrences are of minor importance, all the cellulose made use of being exclusively derived from plants. Formerly we had to content ourselves with such quantities of cellulose as were in a quite pure state at our disposal in the form of vegetable wool and the fibres of textile plants, but the demand for cellulose having acquired colossal dimensions by reason of the enormous increase in the consumption of paper, efforts had to be made to open up other sources of it.

Attention was first directed towards straw as a material for the preparation of cellulose, because it was supposed that its vessels having been only slightly, or not at all, converted into wood, the cellulose could without much difficulty be obtained in a sufficiently pure state. However, it was left out of consideration that the stalks of grasses, which in a dry state form the material termed straw, contain considerable quantities of silica and, in many cases, are provided with what may be called a siliceous armor. This fact frustrated for a long time every attempt to prepare from straw cellulose which might at least be available for the manufacture of paper. Although successful processes for the treatment of straw for paper-making were finally introduced, the pulp obtained as well as the papers manufac-

tured from it, showed so many defects that this mode of obtaining cellulose was soon again abandoned.

The employment of wood for the successful preparation of cellulose in a pure state, and in any quantities desired, is an achievement of modern times, no attempt having been formerly made to utilize this material for the purpose. Chemically, wood is nothing but cellulose which has undergone certain changes. Originally, every kind of wood is cellulose, and in genuine woody plants there is always found around the stalk a growing annular layer which, in accordance with its nature, has to be designated as cellulose. This annular layer, to which the term *liber* has been applied, is formed anew in every period of vegetation, and in the next and succeeding periods of vegetation it is gradually transformed into wood.

This transformation is effected by various bodies, known by the general term of *encrusting substances*, becoming imbedded in the cellulose mass. By this encrustation the originally thin walls of the vessels of which the liber consists, become thicker, more solid, acquire a dark coloration, and are finally transformed into wood-vessels of considerable strength and tenacity, extraordinarily great in some varieties of wood.

The encrusting substances of the wood possess the property of being destroyed or dissolved by various chemicals, while the cellulose is not at all, or but slightly, attacked by them. Hence by one or the other of the processes to be fully described later on, a cellulose is obtained which, when sufficient care has been taken in purifying it, may be called chemically pure, *i. e.*, free from all foreign bodies.

COTTON.

Cellulose as found in nature is never chemically pure, it containing in addition a series of other combinations. In its purest state it occurs in the vegetable structures known as hair or wool. As a rule, each hair consists of a mem-

branous cell, frequently of considerable length, the wall of which is formed of cellulose, admixed, however, with certain salts, nitrogenous combinations, and, in some cases, with coloring matter.

Cotton is, unquestionably, the most important of all the vegetable wools. It is the product of several species of the genus *Gossypium* of the Natural Order *Malvaceæ* or Mallows. The cotton plant has from time immemorial been cultivated in tropical countries. The cotton is found in the fruit of the plant, and actually is the hairs or fibres growing around the seed and attached to it. This attachment of the hairs or fibres to the seed is typical of the genus. The fruit, Fig. 1, known as *boll*, consists of a capsule or pod divided by membranes into three or five cells. It bursts at the time of maturity and the hairs or fibres protrude from it in the form of a compact ball of a white or yellow color. The seeds are the size of a pea and the cotton fibres are separated from them by means of special mechanical contrivances.

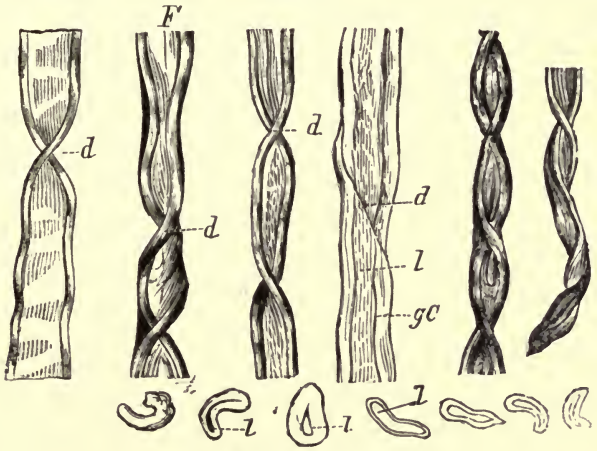
FIG. 1.

Fruit of the Cotton Plant.

Viewed under the microscope, the cotton fibre appears as a hollow cylinder, one end of which is pointed and closed, while the other end, by means of which it was attached to the seed, is irregularly torn. Cotton is the more highly valued the thinner the individual fibres are, the more uniformly smooth they appear under the microscope, and the more closely their form approaches that of a cylinder. Fig. 2 shows cotton fibres highly magnified. As will be seen from the illustration, the individual fibres are more or less strongly twisted and smooth, but with the use of a very high magnifying power they appear obliquely striate.

The length of the cotton fibre varies between 0.391 and 1.575 inches, and its diameter between 0.0004 and 0.0016 inch. In fine qualities of cotton the cavity or lumen of the fibre is quite narrow, while in coarser varieties it is three or four times the size of the cell-wall; in unripe fibres it is sometimes entirely wanting. Like the striation of the fibre, its cuticle can be plainly recognized only with a very high magnifying power.

FIG. 2.



Cotton Fibres.

F, cotton filaments; *d*, places of twist; *g C*, granulated cuticle; *l*, cavity or lumen; *Q*, cross sections.

The value of a variety of cotton is determined by two factors, namely, the length and diameter of the individual fibres; the longer the fibres are and at the same time the smaller their diameter is, the more valuable the cotton. Cotton with fibres less than 0.984 inch long is called *short-staple* as distinguished from *long-staple*, the fibres of which may reach a length of up to 2.362 inches. With regard to the diameter of the fibres, eight different grades of fineness are distinguished in commerce, the limits of diameter for the respective classes being from 0.0004 to 0.0016 inch.

According to numerous analyses, the chemical composition of cotton is as follows: Cellulose 87 to 91 per cent., water 5.2 to 8.0 per cent., fat and wax 0.4 to 0.5 per cent., nitrogenous bodies (remains of protoplasm) 0.5 to 0.7 per cent., ash 0.1 to 0.13 per cent.

In addition to cotton, there are numerous other plants producing fibres consisting largely of cellulose, and which are also used as textile fibres. Among them may be mentioned the fibres of the various species of *Bombax* or wool tree, and of the different varieties of *Asclepias*, but they are far behind cotton in technical importance.

Other natural sources of cellulose-fibres are the bast of a large number of plants, and finally the fibres obtained by a special process (retting) from the stalks and leaves of many plants. As the most important of these may be mentioned: flax, hemp, various kinds of nettle, jute, aloe, Manila hemp, New Zealand flax, etc. For the purpose of preparing from cotton a cellulose which may be considered chemically pure, white cotton is first for some time extracted with ether to dissolve the entire quantity of fat and wax present. It is then repeatedly boiled with soda lye, which, however, should not be too concentrated, whereby the nitrogenous combinations are brought into solution. Very dilute hydrochloric acid is then poured over the cotton and the whole gently heated, the operation being continued for some time. Finally the cotton is treated with water till the last traces of acid have disappeared. When incinerated, cotton, which has been sufficiently purified, should leave no residue.

PROPERTIES OF CELLULOSE.

Cellulose, purified in the manner given above, remains unchanged as regards its structure, chemicals when used in sufficiently dilute state having no effect upon it. The elementary analysis of cellulose leads to the formula $C_{12}H_{20}O_{10}$. However, this formula actually expresses

only its elementary composition, and the actual formula would probably correspond to quite considerable multiples of the numbers above mentioned.

As regards the percentage composition, cellulose agrees with a very large number of other bodies which frequently occur in plants. Thus, it has, for instance, the same composition as starch, gum, gum-like substances, dextrin, etc. These bodies form a large group of isomeric combinations, they having the same percentage composition, but exhibiting different physical and chemical properties.

There can be no doubt that in the living plant-organism these bodies may constantly be transformed one into the other, incontestable proof of this fact being furnished by the bulbs and tubers of many plants. In the cells of such bulbs and tubers large quantities of starch are stored up, but as the development of the plant progresses, the quantity of starch decreases more and more, it being largely transformed into cellulose, gum, etc. Since cellulose may be converted into soluble combinations by the acids formed in plants, it would not seem improbable that, in the higher plants, the chemical process takes place in such a way that a very large number of non-nitrogenous compounds occurring in plants may be directly or indirectly formed from these combinations.

It would also seem very probable that the acids and ferments, which appear during the digestion of nutriment in the stomach, possess the property of transforming cellulose into soluble combinations, because many animals can digest considerable quantities of cellulose, it forming a very important fodder for them. While formerly the opinion prevailed that cellulose is absolutely indigestible for carnivorous animals and human beings, recent researches have shown such not to be the case and that the human stomach is, after all, capable of digesting quite remarkable quantities of it.

SOLUBILITY OF CELLULOSE.

Cellulose is insoluble in ordinary solvents, such as water, alcohol, ether, etc., and, without undergoing a change, actually dissolves only in ammoniacal solution of cupric oxide. When brought in contact with such a solution, the fibres first swell up very much, and solution is then gradually effected. On mixing the solution with alcohol or sugar solution, or neutralizing it with an acid, the cellulose is precipitated in colorless flakes, retaining, however, its original chemical properties.

Formerly no other solvent for cellulose than ammoniacal solution of cupric oxide was known, but towards the end of the 19th century a body also capable of dissolving it was found in the alkaline sulphocarbonates. Solutions of cellulose prepared according to this method exhibit peculiar properties which will without doubt insure their extensive application in various branches of industry. As an example may here be mentioned that textile threads may be prepared from such a cellulose solution.

The behavior of cellulose towards the action of chemical agents is of great importance since a series of combinations of considerable industrial interest may thus be formed.

BEHAVIOR OF CELLULOSE TOWARDS WATER.

At the ordinary temperature water has no effect whatever upon cellulose. In boiled water pure cellulose may be kept for any length of time without suffering any change. If, however, moist cellulose be exposed to the air, the commencement of a change will in a short time be observed, the originally white mass turning gray, becoming constantly darker and finally acquiring the appearance of the black-brown mould found in the rotten core of trees. A microscopical examination of such altered cellulose shows it to contain innumerable bacteria which, in appearance, closely resemble those found in wood mould. This destructive process in cellulose is very probably similar to that which

takes place in the decay of wood, if not entirely identical with it.

That cellulose belongs to the readily changeable combinations is shown by the fact that at a higher temperature it is noticeably affected by water. By boiling pure cellulose with distilled water, for some time in an open vessel under the ordinary pressure, a portion of it is converted into sugar. In water in which pure filter-paper has been boiled, the presence of sugar can be distinctly established.

The action of water upon cellulose is, however, considerably enhanced by boiling for a certain length of time under increased pressure. With a pressure of 5 to 6 atmospheres the cellulose is very noticeably attacked, and the higher the pressure becomes the more energetically the water acts upon the cellulose; with a pressure of 20 atmospheres the cellulose becomes completely hydrated and is changed to hydrocellulose.

However, at this pressure not only hydration of the cellulose takes place, but there appear also other products resembling those which are obtained in abundance in the destructive distillation of wood, especially in the first stages of it; the presence of considerable quantities of formic and acetic acids having been established in water with which cellulose had been treated. In addition, dextrin-like bodies are also formed.

HYDROCELLULOSE.

The combination of cellulose with water, called hydrocellulose, has the composition $C_{12}H_{22}O_{11}$. Hence it differs from ordinary cellulose which has the composition $C_{12}H_{20}O_{10}$ in containing one more equivalent of water. For the preparation of pure hydrocellulose use is made of the energetic action of highly dilute acids upon cellulose even when brought in contact with them at a lower temperature. On a large scale the mode of manufacture is as follows: Mix 3 parts of concentrated sulphuric or hydro-

chloric acid with 97 parts of water, and immerse in the fluid purified cotton—entirely free from fat—until it is completely saturated, which will be the case in at the utmost three to four minutes. The cotton is then taken from the mixture and freed as quickly as possible from adhering fluid, this being best effected by means of a centrifugal apparatus. It is then spread out in a thin layer and allowed to dry completely in the air. The air-dry mass is finally placed in stoneware vessels and heated for three to ten hours at a temperature which should not be below 104° F., and not exceed 158° F.; the higher the temperature the less time is required for heating. The hydrocellulose is then washed with water till the last traces of acid have been removed, and is finally completely dried in the air.

Hydrocellulose has the appearance of the cotton from which it has been prepared, but can be readily rubbed to a very fine powder. It is manufactured on a large scale because it possesses the property, when converted into gun-cotton, of yielding a product which can be more readily exploded by percussion than ordinary gun-cotton, and it is, therefore, preferably used for the preparation of detonating fuses for military purposes.

For the preparation of larger quantities of hydrocellulose, R. Sthamer uses the following process: Chlorine is conducted into glacial acetic acid until the latter is perceptibly colored yellow. It is then heated to between 140° and 158° F., and dry cellulose separated into fibres is introduced while the mass is constantly stirred. The cellulose in a short time swells up very much, so that the mass can scarcely be stirred, hence three to five parts by weight of acetic acid should be used to one part by weight of cellulose. The mass at first increases constantly in volume, but after some time it sinks down, and is finally transformed into a thin paste which is washed with water and dried. Care must be taken not to allow the temperature to rise

above 158° F., as otherwise oxidizing processes may take place in the mass, and the hydrocellulose would not exhibit a pure white, but a brownish color.

In place of glacial acetic acid, hydrochloric acid, which is cheaper, may also be used for the preparation of hydrocellulose, the process, according to Sthamer being as follows: Bring into a vessel provided with a steam jacket and a stirring apparatus, 200 lbs. of cellulose in fibres and add, with constant stirring, 1600 to 2000 lbs. of crude hydrochloric acid of 21° Bé., keeping the temperature at 158° F. A small quantity of finely pulverized potassium chlorate—about 0.5 to 0.8 oz. at a time—is from time to time added to the mass. When in the course of about $1\frac{1}{2}$ hours a total quantity of 2 lbs. of potassium chlorate has been added, the formation of hydrocellulose may be considered finished, the end of the reaction being recognized by the uniformly pasty nature of the mass. The hydrochloric acid is whirled out by means of a centrifugal apparatus, and may be used for the next operation. The hydrocellulose is then washed and dried. The time required for finishing the process depends largely on the nature of the cellulose used, a fine-fibered material requiring less time than one with close and tough fibres.

Hydrocellulose prepared with the use of potassium chlorate is said to be distinguished by very great chemical indifference towards acids and lyes, and its use for the manufacture of articles which come in contact with them is especially recommended by Sthamer.

BEHAVIOR OF CELLULOSE TOWARDS ACIDS.

While in the presence of even small quantities of acid, especially of strong inorganic acids, the action of water upon cellulose is very much enhanced, the acids themselves do not enter into combination with the products formed. Hence it may be supposed that by the action of the acids upon the cellulose certain combinations are

formed which, however, are again immediately decomposed so that the liberated acid can act upon a fresh quantity of cellulose. If this supposition is correct, the phenomenon of the mere presence of minute quantities of acid being sufficient to change an almost unlimited quantity of cellulose is readily explained.

The behavior of cellulose towards acids varies according to the kind of acid, its concentration, and duration of its action. Highly diluted sulphuric acid has no effect whatever, even if left for a long time in contact with cellulose, but when boiled with it for some time, the cellulose is partly transformed into fermentable sugar. Upon this behavior are based various processes for the preparation of alcohol from cellulose or wood. The fluid obtained by boiling cellulose with dilute sulphuric acid is neutralized with lime and brought into alcoholic fermentation with yeast. The process has the appearance of being a very simple and obvious method of manufacturing alcohol, nevertheless in practice a number of difficulties are encountered, so that hitherto very little use has been made of this property of cellulose.

When cellulose, best in the form of unsized paper, is for a few seconds immersed in concentrated sulphuric acid, and the acid is then quickly removed by washing in a large quantity of water, it undergoes a profound physical change. The paper by this treatment acquires great strength, and in appearance resembles parchment. By treating paper with concentrated solution of zinc chloride, a product resembling parchment is also obtained.

Cellulose is completely dissolved if allowed to remain for some time in contact with cold concentrated sulphuric acid. If, in a short time after solution is complete, the fluid be diluted with water, a colorless body having the composition of cellulose is separated and which, from its resemblance to starch, has been termed *amyloid.*

If solution of cellulose in concentrated sulphuric acid be

allowed to stand for some time, the cellulose is completely converted into dextrin.

However, when boiled with concentrated sulphuric acid, cellulose is entirely decomposed, and by reason of its carbonization imparts to the fluid a deep black color. The sulphuric acid is also decomposed, as shown by the development of sulphur dioxide from the hot fluid.

Generally speaking, the action of hydrochloric acid upon cellulose is similar to that of sulphuric acid, its effect, however, being less energetic, and in boiling cellulose with it no carbonization takes place.

Sulphurous acid acts quite energetically, especially with the use of higher pressure, and converts cellulose partially into fermentable sugar.

By organic acids, such as tartaric, citric and acetic acids, cellulose is but slightly attacked, they acting somewhat more energetically when in a concentrated state; oxalic acid produces the most vigorous effect.

Nitric acid effects profound chemical changes in cellulose, the nature of the products formed depending on the concentration of the acid used and the duration of its action. Cellulose esters or cellulose nitrates or nitro-cellulose are formed, a group of combinations which are especially distinguished by their power of exploding with great force and dissolving in various bodies. However, notwithstanding the profound chemical change, nitrated cellulose exhibits no difference in its physical structure. Under the microscope it presents the same appearance as non-nitrated cotton, but differs from it essentially in its behavior towards polarized light.

The acid sulphites of the alkalies and alkaline earths attack cellulose only to a very limited extent, but they act all the more vigorously upon the encrusting substance of the wood. The same is the case with free chlorine, and the action of the sulphites and of chlorine (the latter in the electro-chemical process) is made use of in the preparation of cellulose from wood.

Cellulose also forms with a number of organic acids, such as acetic acid, butyric acid, etc., combinations which possess the characters of esters. These combinations, which have only recently been discovered and investigated, show properties which lead to the expectation that they may also be of industrial importance, though at present they only have been experimented with on a small scale.

BEHAVIOR OF CELLULOSE TOWARDS ALKALIES.

The caustic alkalies—caustic potash and caustic soda—when allowed to act for a short time produce a favorable change in cellulose, the fibres becoming more compact and solid, so that fibres, especially those of cotton thus treated, can be more readily dyed and acquire a more beautiful color than the ordinary material.

When concentrated solutions of caustic alkali—caustic potash or caustic soda—are for a short time allowed to act upon cellulose (cotton) the fibres undergo a peculiar change. Fibres thus treated, when viewed under the microscope, appear very much swollen, their cross sections are much enlarged and nearly circular, and the cavity in the interior is so much smaller that it can scarcely be recognized; the twist of the fibre is also considerably increased.

By this treatment the fibres become also more solid and firmer and in dyeing behave differently from ordinary materials. With the use of the same dyeing liquor they acquire a much fuller tone of color, and the same result is obtained with smaller quantities of coloring matter than otherwise would be possible.

This peculiar behavior of the cotton fibre was discovered by John Mercer and introduced by him in the practice of cotton dyeing. The term *mercerization* has been applied to the process, and it is much used at the present time.

By treating cellulose with highly-concentrated solution of caustic alkalies it is largely converted into oxalic acid.

By treating cellulose with a suitable quantity of caustic

soda and then adding to the mass a certain quantity of carbon disulphide, a thickly-fluid solution is obtained which is distinguished by an extraordinary adhesive power. By heating, the solution is again decomposed, whereby the carbon disulphide is volatilized and the cellulose passes again into an insoluble form.

BEHAVIOR OF CELLULOSE AT AN INCREASED TEMPERATURE.

Cellulose exposed in a close vessel to a higher temperature commences to decompose at about 302° F., and when the temperature is constantly increased there remains finally a lustrous black coal. By this heating, or destructive distillation as it is called, various products, partially gaseous, partially fluid or solid, are formed. The gaseous products form to upwards of 30 per cent. of the weight of the cellulose, and consist chiefly of varying quantities of carbonic acid and carbonic oxide. The fluid products separate in two layers, one of them being of an aqueous nature and amounting to about 40 per cent. of the weight of the cellulose, while the other represents a thick, viscous mass—the so-called wood tar—of a dark brown, nearly black, color, which amounts to from 4 to 6 per cent. of the weight of the cellulose.

The aqueous fluid, the so-called wood vinegar, contains, besides water, considerable quantities of acetic acid, acetone, methyl alcohol, small quantities of butyric acid and other combinations. The wood tar consists of a large series of hydrocarbons which are partially fluid or of an oil-like nature, while other constituents, to which belongs paraffine, are at the ordinary temperature solid and crystalline.

It will be seen from the brief explanations given above of the behavior of cellulose towards the action of chemicals and of the effect of higher temperatures upon it, that it forms the basis-material of a large series of combinations of great technical importance. In the forms in which it is yielded by the so-called textile plants, it constitutes the

chief material of the textile industry and partially supplies the material for the manufacture of paper, though for the latter purpose the artificial product furnishes an exceedingly valuable substitute. Cellulose is further used in the manufacture of most of the blasting materials and explosive bodies, for the preparation of viscose, celluloid and several other substances, and it may, therefore, be properly called one of the most important raw materials of the textile and chemical industries.

INDUSTRIAL USES OF CELLULOSE.

Cellulose and its derivatives are used for many purposes, and the object of the enumeration here given is simply to show in a comprehensive manner the great importance of these bodies for the various industries.

Pure cellulose as at present prepared from wood is most extensively employed in the manufacture of paper and considerable quantities of it are also used for the manufacture of fire-proof paste-board for roofing (*carton pierre*), for the preparation of plastic masses, and as an excellent filter material.

The term *vegetable parchment* has been applied to cellulose in the form of paper which has been changed by subjecting it for a short time to the action of concentrated sulphuric acid. On account of its strength it is used for book bindings, as well as a dialyzer in various chemical industries, for instance, in the manufacture of sugar.

Cellulose sulphocarbonate or viscose is used as a sizing material for dressing tissues, as a thickening substance in calico-printing and for the preparation of textile threads. In the course of time, it very likely will also be applied to other purposes. Solutions of pure cellulose in cuprammonium are at present used in a similar manner to viscose for the production of textile threads.

To the important derivatives of cellulose belong the combinations to which the general term of *nitrocelluloses* has

been applied. Some of these combinations are distinguished by great explosive power and are extensively used for the preparation of blasting agents, while others, which are soluble in certain fluids, form with them the so-called collodion which is used in surgery and photography and, in modern times, also for the preparation of textile threads to which the term *artificial silk* has been applied.

The peculiar substance formed by bringing together nitrocellulose with certain hydrocarbons and known as *celluloid* has found many applications in the industries and arts.

The general suggestions which have here been made as to the utilization of cellulose and its derivatives suffice to prove that they belong to the most important bodies available to the industries.

The conversion of cellulose into fermentable sugar, and of the latter into alcohol, being actually possible, it is not unlikely that some time or another in the future a process will be perfected by means of which the production of alcohol from cellulose, relatively wood, will be more profitable than from plants containing starch. Since alcohol itself forms the initial material for the preparation of many other chemical products, such as ether, vinegar, etc., a new field for the utilization of cellulose would be opened and the import of the invention of a suitable process for the production of alcohol from wood can scarcely be estimated. Present experiences in this line, though encouraging, are not sufficiently perfected for their application on a large scale. However, it may be fairly asserted that the rational preparation of alcohol from wood is only a question of time.

PRODUCTION OF CELLULOSE.

Up to modern times—about the first half of the nineteenth century—no other sources for cellulose than certain parts of plants were known. In warmer countries where

the cotton plant thrives, the hair which grows around the seed and which consists almost of pure cellulose, formed the material for the preparation of textile threads. In countries having a colder climate, flax, as well as hemp, has from time immemorial been the principal source of cellulose fibres.

In addition to the plants mentioned above, a number of others were to a more limited extent utilized in other parts of the globe for the production of cellulose. However, the use of such plants was merely local, while that of cotton, flax and hemp was universal.

Since communication with cotton-producing countries has been greatly facilitated, this material has been generally adopted in Europe and has in many cases displaced flax for the production of textile fibres.

Paper consists of cellulose fibres felted together in a peculiar manner, and formerly linen rags were exclusively used for its manufacture. In consequence of the enormous increase in the consumption of paper the price of rags advanced constantly, and it became necessary for the paper manufacturer to find other sources of cellulose suitable for his purposes.

It had for a long time been known that unlimited quantities of cellulose were available in the higher plants, the larger part of their tissues consisting of it. However, this cellulose occurs in such a form that no means were known by which it could be separated in a suitable shape for the manufacture of paper.

The first experiments made in this direction were for the purpose of obtaining the cellulose contained in the straw of the various kinds of grain. The results of these experiments were, however, satisfactory only in so far that a material was obtained which at the best was only suitable as an addition to the cellulose mass prepared from rags. When used by itself for the manufacture of paper, the resulting product was of a very inferior quality as to appear-

ance and solidity. A substance suitable for the manufacture of paper was obtained from maize straw and yielded somewhat better results, Alois Auer, formerly director of the Austrian government printing-office at Vienna, deserving special credit for his efforts in this respect.

As might be expected, many experiments were made for the purpose of obtaining the cellulose contained in wood, but none of them was successful because no means were known to bring into solution the encrusting substance by which the individual vascular bundles are cemented together.

However, the production from wood of a material which would at least serve as a partial substitute for cellulose, in the manufacture of paper was finally successfully accomplished, though the paper made from it was inferior in quality to the product from pure cellulose.

This substitute consisted of wood reduced to a more or less fine condition by mechanical means. The reduction was effected by means of grindstones, and large works for the manufacture of this material were established. However, this wood pulp prepared by mechanical processes was nothing but wood, and could only be mixed in certain proportions with the pulp prepared from rags, and the resulting paper was of an inferior quality. It was brittle and its color was not pure, and by exposure to light soon turned brownish. It constituted, however, a valuable material for newspapers and other printed matter intended for temporary purposes. In the manufacture of paper, wood-pulp prepared by mechanical means is at present only used for very ordinary grades; it is, however, extensively used in the manufacture of paste-board.

By the efforts of chemists a process was finally found by means of which it was rendered possible to prepare from wood pure cellulose of such a quality as to be suitable for the better grades of paper, and from this period on dates a great revolution in the manufacture of paper.

A process was discovered by which the complete solution and destruction of the lignin or encrusting substance of the wood is made possible, so that the individual vascular bundles are deprived of their coherence and fall apart, and after removing the solvent and bleaching, appear as pure cellulose.

Thus far only two groups of bodies are known which may be used for the destruction of the encrusting substance, namely, the caustic alkalies, alkaline sulphites, and chlorine, and one or the other group of these combinations is employed in every process, no matter under what name it may be known, for the preparation of cellulose.

To judge from the present state of the industry, the question as regards the preparation from wood of cellulose suitable for the manufacture of paper would, therefore, appear to be solved. However, there remains the solution of a no less important problem, namely, the production from wood of cellulose of such a quality as to render it suitable for the preparation of textile threads. Many experiments have been made in this direction, but without entirely satisfactory results, it having thus far been only possible to make cellulose threads a few millimeters long, while fibres of considerably greater length are required for textile purposes.

There can scarcely be any doubt that this question will also be solved in the course of time, and we will then have in wood-cellulose a material available for the manufacture of paper, as well as for weaving tissues, and which will to a considerable extent be detrimental to the cultivation of cotton and flax.

With reference to what has been said above, two phases of the historical development of the production of cellulose from wood will have to be kept in view, the one in which the efforts were directed towards the preparation by mechanical processes of a material suitable for the manufacture of paper, and the other, in which the efforts led to

the production of pure cellulose from wood. According to the nature of the chemicals used, the manufacture of cellulose may be divided into that of soda-cellulose, sulphite-cellulose and electro-chemical-cellulose.

As has been previously mentioned, the problem of producing textile threads from wood has thus far not been satisfactorily solved, though such threads are at the present time made in a roundabout way from cellulose. As this subject will be fully discussed later on, it need here be only briefly referred to. From wood, pure cellulose can only be obtained in the form of short fibres, but fluids are known in which the cellulose dissolves without undergoing a change as regards its physical and chemical properties. These solutions can be converted into very long and extremely thin threads, from which the cellulose can be separated so that it retains all its original properties. Threads thus produced may be spun into yarn like other textile fibres and from such yarn fabrics can be made which do not differ from other cellulose tissues, except that they present a more beautiful appearance as regards smoothness and lustre. It will thus be seen that, even at the present time, cellulose from wood may actually be obtained—though in an indirect way—in the form of textile fibres.

II.

WOOD-STUFF, OR MECHANICAL WOOD-PULP.

The term wood-stuff or mechanical wood-pulp, is applied to wood converted by purely mechanical means into a fine-fibred mass, which by itself may serve for the production of coarser grades of paste-board, as well as for the manufacture of various articles. Its chief use, however, is as an addition to paper stock for the manufacture of inferior grades of paper. Although wood-stuff, if properly prepared, is sufficiently fine-fibred to be made into paper in the paper machine, it is not used by itself for this purpose, because such paper possesses the disagreeable property of becoming darker, and acquiring in a short time a brown coloration when stored exposed to the light. The cause of this phenomenon is found in the fact that the wood-stuff still contains nearly the entire quantity of encrusting substance, lignin, etc., originally present in the wood, these substances being subject to great changes. Hence, in the course of time efforts were made to remove these substances from the wood, so that only pure cellulose remains behind, which, as it does not show the above-mentioned defects, can be used by itself for the manufacture of paper.

The process of grinding wood has been known for a comparatively long time. The fundamental idea originated with F. G. Keller, of Hainichen, Saxony, and was so far perfected by him in conjunction with Heinrich Voelter, of Heidenheim, Wurtemberg, that as early as 1846, the first patents for wood-grinding processes were granted. In the second half of the 19th century, wood-grinding processes were introduced in all countries abounding in varieties of

wood suitable for the purpose, and the bulk of paste-board, as well as that of ordinary newspaper, is made from ground wood.

Voelter's process of wood grinding is executed as follows: Suitably prepared blocks of wood are pressed against a rapidly revolving grindstone which is kept constantly wet by water. By the grindstone the wood is reduced to a mixture of fine fibres, larger shreds, quite large shavings, and water. This mixture is first caused to press against a quite coarse wire screen which retains the coarser shavings and splinters. From this screen the mass is led through a series of cylindrical screens covered with wire gauze increasing in fineness, so that from the last screen a thin paste consisting of the finest wood fibre and water runs off. The separation of the wood fibres from the water is effected in various ways, it being frequently accomplished by allowing the paste to flow over an endless fine-meshed metallic cloth. The water runs off through the meshes while the fibres in the form of a delicate pulp remain upon the cloth, and may be still further freed from water by rolls. In this case, the pulp is very frequently conducted at once to the rolls of the paper machine where it is converted into sheets of fixed size. According to another method, the pulp is allowed to drain off in large boxes and is then freed from water by pressing.

WOOD FOR GRINDING.

Although every kind of wood may be ground, the different varieties are by no means alike suitable for the purposes for which the pulp is to be used. Of the European varieties of wood, asp, linden, fir, pine and birch are especially well adapted for the purpose, while beech is less suitable. In America the soft white wood of the tulip tree (*Liriodendron tulipifera*) commonly called poplar, as well as the wood of spruce and pine, is used in large quantities for mechanical wood-pulp.

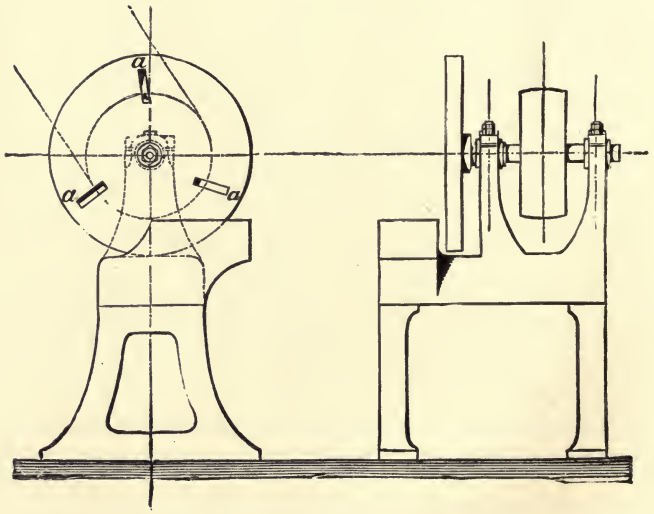
The soft white woods of the asp and linden yield a beautiful white pulp, which, however, does not act to advantage in the paper-stuff, paper prepared with such pulp turning out soft and spongy. The pulp from pine or fir, to be sure, is not quite so white, but can be worked into firm, smooth paper.

Before being subjected to the grinding process the wood must be carefully examined and prepared. Decayed or rotten wood should be absolutely rejected since the resulting pulp would have a brownish color, and when allowed to lie for some time in a moist state would become mouldy throughout. Hence only sound, clean wood should be worked.

PREPARATION OF THE WOOD TO BE GROUND.

The preparation of the wood for the grinding process is effected by means of special machinery. The blocks of

FIG. 3. FIG. 4.

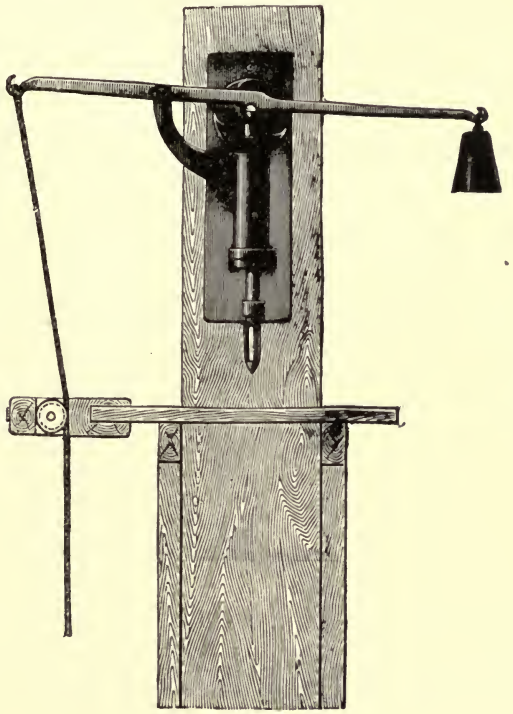


wood are first submitted to a machine, which is a sort of revolving plane, and cuts away the bark. Such a machine

is shown in front and side views in Figs. 3 and 4. As will be seen from Fig. 3, three knives are fixed to the rapidly revolving drum. By conducting the blocks of wood against these knives, the bark is cut away, care being taken to see that it is completely removed, otherwise the pulp will inevitably show dark spots.

Since knotty wood cannot be properly ground, the knots

FIG. 5.



have to be removed, various kinds of machinery being used for this purpose. A machine of simple construction is shown in Fig. 5, the removal of the knots being effected by means of a rapidly revolving auger. Another machine for the purpose, Fig. 6, is furnished with a spoon-shaped

auger, which is set in rapid motion by the bevel gear, Fig. 7.

The blocks of wood thus prepared are cut by means of a circular saw into pieces of such a length that they can be laid in the individual pockets of the grinding apparatus. Each block is finally split into at least two pieces by means

Fig. 6.

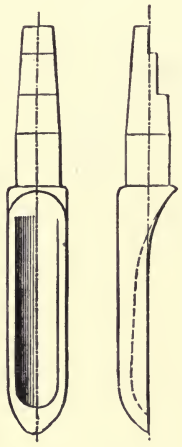
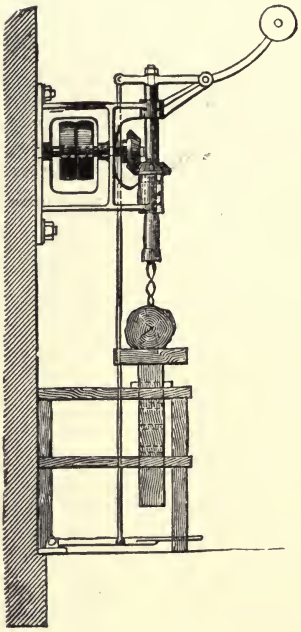


Fig. 7.



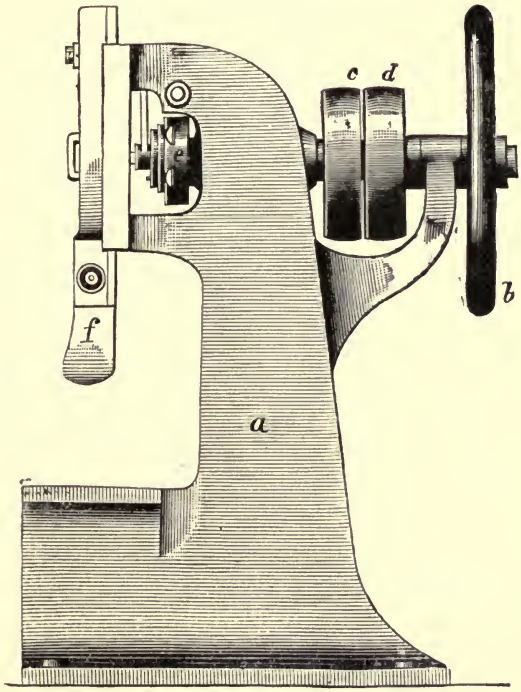
of a splitting machine, Fig. 8. The chief object of this splitting is not so much to chop up the wood as to give an opportunity for examining it inside, since many blocks appearing perfectly sound from the outside may be rotten at the core, and hence of no use for the preparation of pulp.

When the wood has been thus freed from bark and knots, and on splitting been found to be sound throughout, it is ready for the grinding machine.

WOOD-GRINDING MACHINES.

Every kind of machine for grinding wood consists of a grindstone, generally of fine-grained sandstone, which revolves with great velocity around its axis, and against the surface of which the wood is pressed, the latter being kept constantly wet with water. The wood is placed so that its vascular bundles lie parallel to the surface of the grindstone. The latter in revolving tears from the wood indi-

FIG. 8.



vidual vascular bundles, as well as entire groups of them, and not seldom even larger splinters. The mass torn loose is carried by the water into a vat, in which the revolving stone is placed, and from there to the sorting contrivances, by which the different-sized particles of wood are separated one from the other.

The oldest of these machines is that constructed by Voelter, and it has proved so satisfactory that up to the present time it has undergone but slight modifications, its main features remaining the same.

In Voelter's, as well as in other machines built in imitation of it, the grindstone is fixed to a horizontal shaft, but in some more modern constructions, to a vertical shaft. However, a horizontal position of the shaft is considered more suitable by all who have had the opportunity to test the capacity of the different machines.

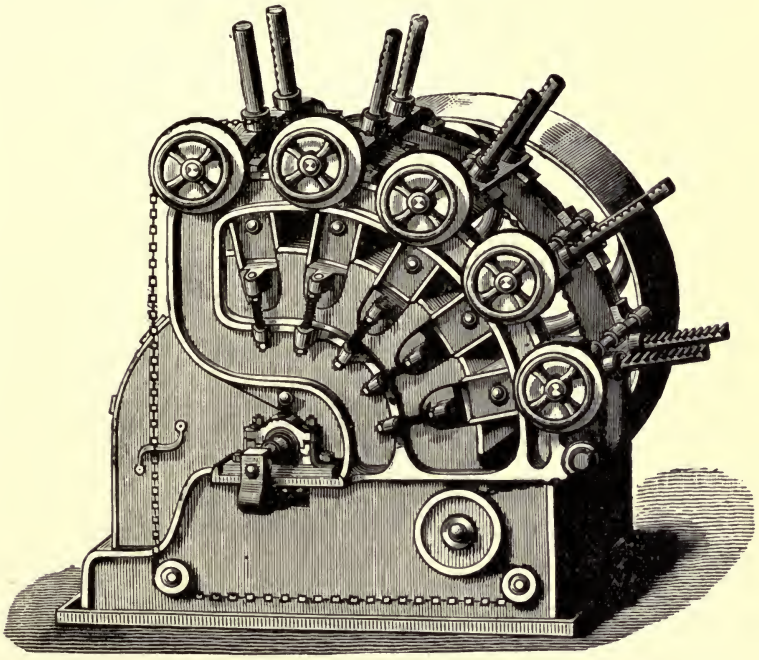
VOELTER'S GRINDING MACHINE.

Voelter's grinding machine, Fig. 9, consists of a frame having two strong, cast-iron sides firmly bolted together and supporting the bearings of the grindstone. One side of the frame is so arranged that the sheet-iron jacket can be removed so as to allow of the grindstone being readily exchanged without the necessity of taking the entire machine apart. Between the two sides, fixed to their surfaces, are pockets or boxes, in which the wood to be ground is placed. The blocks of wood are pressed against the grindstone by a spur gearing, uniform pressure being kept up by means of a tight endless chain. The arrangement of this mechanism is such that when one pocket becomes disengaged, the others receive a somewhat stronger pressure, the uniform running of the machine being thus constantly maintained, and one or two pockets may be refilled without stopping the machine.

The grindstone is somewhat wider than the blocks of wood to be ground, and is furnished with a mechanical contrivance by means of which, while it revolves, it can alternately be shifted towards the right and the left. The effect of this arrangement is that not only the stone wears more uniformly, but its disintegrating action upon the wood is also increased. The pockets in which the wood is placed have the form of truncated pyramids. Each pocket

is provided with a strong, cast-iron cover which is pressed down by the racks connected with the spur wheels, the latter being constantly drawn down by the endless chain. When a pocket has been filled with wood, the cover is placed in position and, by engaging the spur wheel, is firmly pressed upon the wood, and the latter is then submitted to the grinding action of the stone. Each pocket is

FIG. 9.

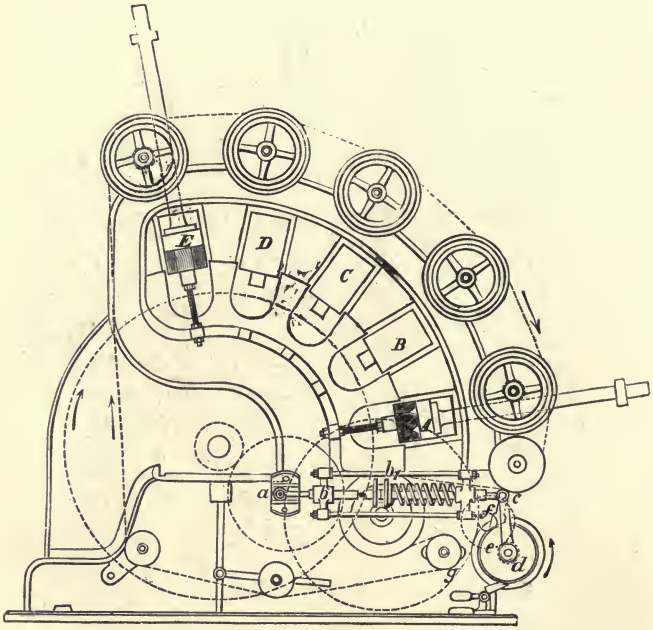


furnished with a pipe through which an abundance of water is constantly conducted over the wood and the stone. The fragments of wood detached by the stone, being immediately washed away, fall to the bottom of the vat, and are carried to the sorting screens. As the water is generally introduced in fine jets under high pressure, the detached particles of wood are sure to be washed away by the force

thus brought to bear upon them, and there is no danger of the machine becoming clogged by splinters.

There are numerous constructions of machines in which the grindstones are placed vertically, but in principle they do not differ from Voelter's machine. Some of them, however, show certain improvements as regards the mode of pressing the blocks of wood against the grindstone.

Fig. 10.



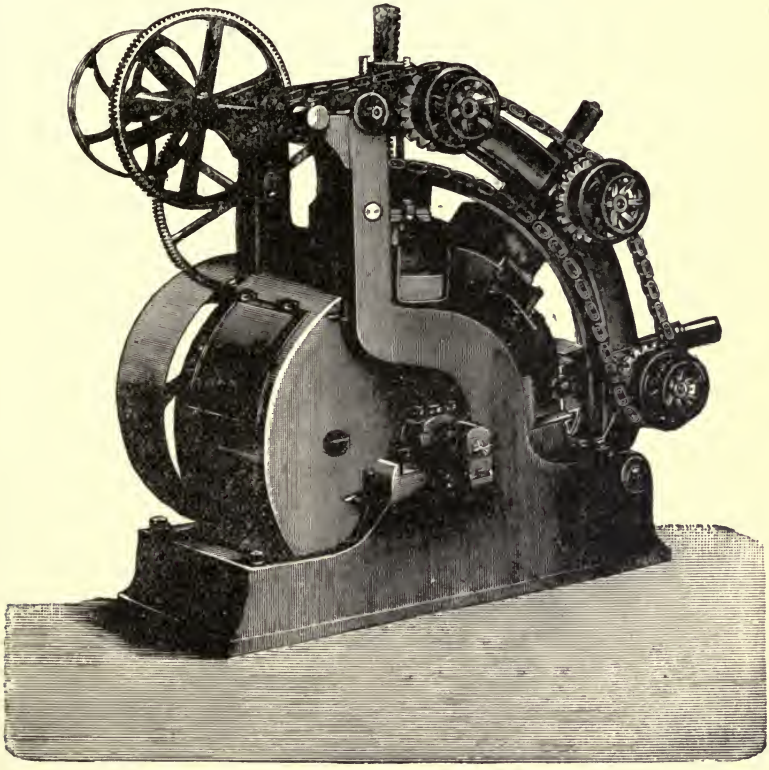
A. Oser's machine, Fig. 10, is so arranged that a constant and adjustable pressure upon the blocks of wood by the endless chain is produced by means of a movable crank, *a*, which receives its impulse from the shaft of the stone, further by the spring-connecting rod, *b*, the contrivance for engaging the binding attachment, *c*, and the connecting gear, which is set in motion by the wheels, *d e* and *f g*.

Fig. 11 shows Voith's wood-grinding machine, which differs but little from the one described above.

FREITAG'S GRINDING MACHINE.

This is an original construction of a grinding machine with stones fixed to a perpendicular shaft. Four or five

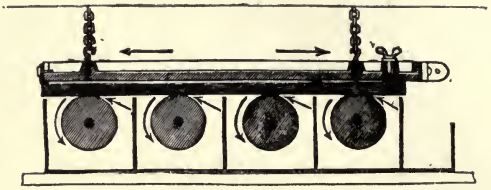
FIG. 11.



grindstones, each having a diameter of only about 20 inches, are used, and their bearings are so arranged that the surfaces of all the stones can be adjusted at exactly the same height. The wood to be ground, in the form of a long block, Fig. 12, is laid upon the stones, pressed against them

by means of an iron plate, and, during the process of grinding, is to a fixed extent moved to and fro. This grinding

Fig. 12.

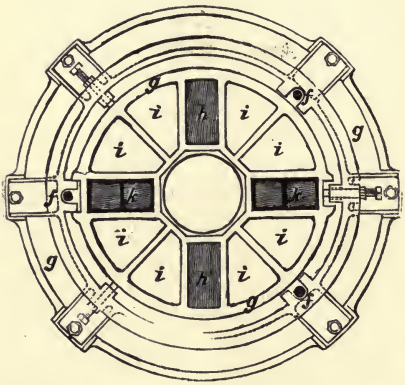


apparatus is said to furnish especially long fibres which is certainly of great advantage for the quality of the pulp.

Abadie's Grinding Machine.

Of an entirely different construction are the wood-grinding machines in which one of the circular surfaces of the stone is used as the grinding plane, as is the case in the machine constructed by August Abadie. This machine, Figs. 13 and 14, is furnished with four press-pockets, *h*, the pistons of which are loaded with the weights, *k*. The load may be increased by the use of the connecting gears fixed above *k*, which serve also for raising the press-pockets when they are to be refilled. In the spaces *i* between the press-pockets, weights of iron, stone or wood are to be placed, their object being immediately to grind up the wood-stuff detached by the grindstone. This specification, however, has yet to be proved by direct experiments.

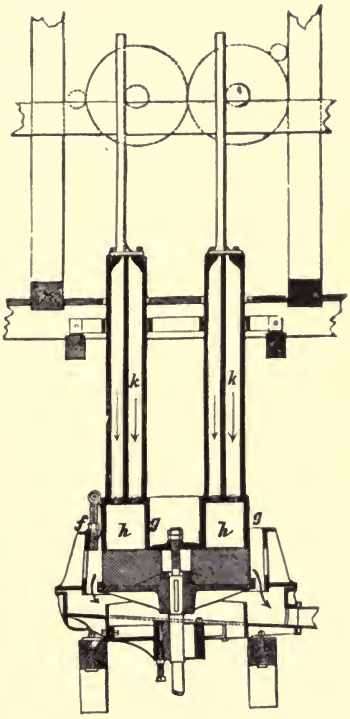
Fig. 13.



It is a matter of experience that the wood-stuff detached

from the blocks of wood in one press-pocket, should as rapidly as possible be withdrawn from the further action of the machine, since the fibres, when dragged again into another pocket and there again exposed to the action of the grindstone, are too much reduced or what is technically called *dead-ground*. This contingency need not be feared in Abadie's machine, since the water is supplied from the centre of the machine so that it is forced outward by centrifugal force and immediately carries away all the particles of wood lying in its course. The individual pockets or presses are fixed in a frame *g*, and the latter is pressed firmly against the grindstone by three perpendicular screws *f*, and accurately centered by three horizontal screws.

Fig. 14.



In addition to the constructions above described, there are a few other wood-grinding machines in which the stone is fixed to a vertical shaft, so that its entire surface may be set with press-pockets. In an apparatus of this kind, constructed by Liebrecht, eight grinding pockets in all are used, and the wood is pressed against the grindstone by hydraulic pressure. Such a machine, of course, can in the same time work up a larger quantity of wood than one with only four or five grinding pockets, but it must also be borne in mind that the consumption of power is correspondingly greater and that the grindstone is subject to much greater wear.

Regarding the use of hydraulic pressure for pressing the wood against the grindstone, Liebrecht's construction in this respect must be acknowledged as a very ingenious one. However, the apparatus becomes, thereby, more expensive and more complicated, two factors which are not in favor of a machine on which heavy demands are made.

In construction, Voelter's wood-grinding machine is more simple than any other apparatus for the same purpose, and the unexpected giving-away of any important part can scarcely happen; furthermore, the grindstone can be readily removed and in a short time replaced by another one. With this machine, as shown by practical experience, operations can be carried on for a long time without having to stop work for more extensive repairs.

WATER USED FOR GRINDING.

Regarding the water which during the grinding operation has to be constantly conducted upon the grinding surface, it may be mentioned that it should be perfectly clear and free from suspended solid bodies—especially sand or clay. Such bodies would, of course, adhere to the pulp and affect its purity, this being especially the case with particles of clay contained in the water used. Pulp from a variety of wood which otherwise would yield a nearly white product, acquires by a content of clay—according to the color of the latter—a yellow or gray appearance.

Hence, when in the locality where a grinding plant is to be established, perfectly clear water, free from sand or clay, is not available, it would seem advisable to pass the water required for grinding through a filter which retains the suspended solid bodies. In order to economize, in this case, with filtered water, the water running off from the sorting screens is not allowed to flow away, but is collected in a basin and pumped into a reservoir placed at a higher level, from which it is reconducted to the grinding apparatus.

SORTING THE GROUND MASS.

The operation subsequent to the grinding process consists in separating the different-sized particles detached by the grindstone from the blocks of wood. The general term *sorters* is applied to the various contrivances used for the purpose.

Before commencing the actual sorting operation, the fluid coming from the grinding apparatus is passed through the so-called splinter-catcher. The latter consists of a larger vessel in which sits a cylinder with slit sides, or covered with a wire screen. The cylinder revolves slowly around its axis and frequently is also kept in an oscillating motion. The particles of wood, which are small enough to pass through the slits or meshes of the cylinder, are carried, together with the water, to the sorters, whilst the coarser splinters collect in the box of the splinter-catcher, to be further reduced in special mills.

The sorters, which serve for sorting the wood-stuff, resemble in the main other appliances used for similar purposes. They consist either of a series of sieves of gradually increasing fineness which are kept in a shaking motion, or of revolving cylinders covered with wire sieves. In place of revolving cylinders, hexagonal prisms covered with wire sieves are also used.

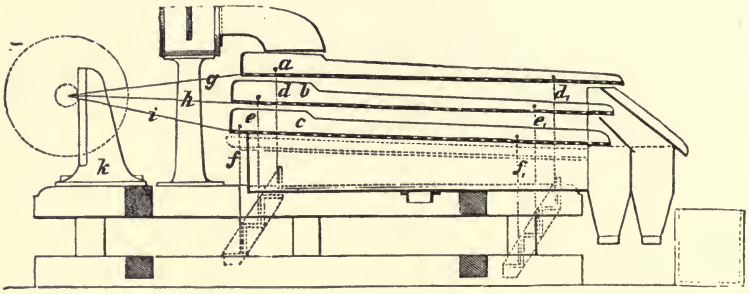
Voith's shaking sieves are shown in Figs. 15 and 16. The sifting frames consist of sheet iron, the ends being turned up. Each frame rests upon four steel springs, *d*—*d*, *e*—*e* and *f*—*f*, and is connected with a spring-connecting rod, *g h i*. The cranked axle lies in *k l*, its crank-pins being placed one against the other at an angle of 120°, whereby, in connection with the fly-wheel, a quite uniform running of the machine is attained.

The sieves are kept in a very rapid jerking or shaking motion—400 to 500 motions per minute. By the use of springs, as applied in the above-described machine, the otherwise great wear and tear of the machine is reduced

and the very loud noise made by the shaking sieves is considerably modified.

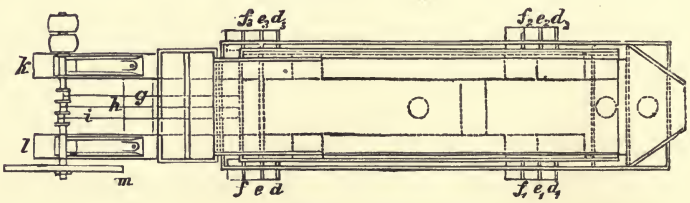
The mode of operation of the shaking sieve is a very simple one: The mass, consisting of particles of wood and water which comes from the splinter-catcher, falls upon the

Fig. 15.



uppermost sieve. Water and all particles of wood smaller than the meshes fall through the sieve, whilst the coarser particles slide down over it and collect in a receptacle. The same process is repeated in the succeeding sieves, and a pulp of delicate particles of wood and water runs finally from the lowest and finest-meshed sieve into the settling vat.

Fig. 16.



With the use of cylinder-sieves the same process takes place in a revolving cylinder, in which the mass coming from the splinter-catcher is freed from the coarser particles, then passes to the succeeding narrower-meshed cylinder-sieve, and so on. Instead of arranging three or more

cylinder-sieves one after the other the sieves may also be fixed one inside the other so that they revolve towards each other in opposite directions, the second revolving in an opposite direction to the first outermost, and the third again in the same direction as the outermost.

The mass coming from the splinter-catcher passes into a trough into which the outermost sieve dips, and being carried along by it, reaches the second sieve, and from this finally the innermost one.

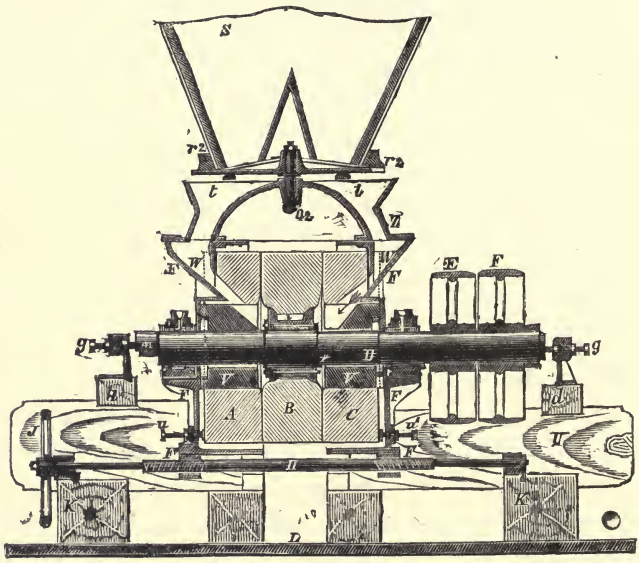
The particles of the ground wood which have passed through the sieve with the narrowest meshes are considered of sufficient fineness not to require further manipulation. Hence this pulp is directly conducted to the settling vats, the dehydrating apparatus or the board machines.

The particles of wood which are not sufficiently ground have to be further reduced, the simplest manner of accomplishing this being by means of mill-stones of ordinary construction. However, special mills which are better adapted for this purpose have also been constructed. Such a mill, known as a *refiner*, is shown in Figs. 17 and 18.

This mill differs from the ordinary constructions in being furnished with two stationary millstones placed in a vertical position, between which revolves a runner dressed on both sides. Since this stone possesses two grinding planes, the same performance can be attained with one stone of small diameter as with much larger stones in an ordinary mill. In the illustrations, *A*, *B*, *C* represent the three stones, the middle stone *B* being fixed by means of a box-screw to the shaft *D*. The stones *A* and *C* sit upon the carriage *F F*, and are firmly fixed to it by the screws *u* and *u*. *Z* is a jacket enclosing the stones, and the carriage *F F*, together with the stones, can be shifted in it. The shifting of the stones for the purpose of regulating the distance between them is effected by means of the wheel *J*. Both stones are simultaneously shifted upon the support *Z*, the shaft *H* being furnished with a left and right thread. *S* represents

the contrivance for the introduction of the wood. It is fixed to the jacket *Z* by means of the iron supports *r r*, and terminates in two outlets *t t*. *S* is a gutter also furnished with two outlets, so that the wood to be ground reaches the grinding surface by means of *t t*, the channels *W W*, and the two exterior sides of the stones, the latter receiving it only upon the lower halves of their circumferences. The wood remains between the stones only long enough to be

Fig. 17.

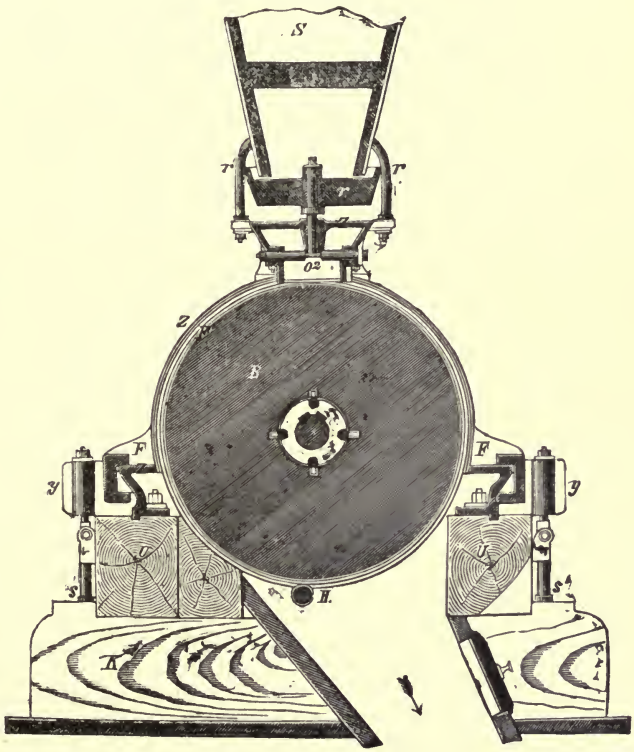


reduced to a degree of fineness corresponding to the distance between the stones, when it falls down on its own account.

In place of the refiner, finely corrugated rolls may be used for the reduction of the particles of wood. They revolve with different velocities whereby the wood is at the same time torn and crushed. The wood thus reduced is, for the sake of precaution, passed through a fine-meshed sieve in order to retain coarser particles which may have escaped the action of the mill, and finally reaches the con-

trivances for the separation of the pulp from the water. These contrivances consist of revolving cylinders covered with fine gauze-wire sieves so that the water, but not the pulp, can pass through. By this means, the pulp, to be sure, loses considerable water, but is not sufficiently freed from it, the use of special apparatuses being required for

Fig. 18.



the complete removal of the water as far as it is at all possible.

The water running off from the dehydrating cylinders always carries with it a certain quantity of the finest particles of the pulp which is sought to be recovered in various ways, sieves of the finest gauze wire being most frequently

used for the purpose. The water flows over the sieve while the air is exhausted underneath it. The water penetrates through the meshes while the pulp remains upon the sieve, and is removed from it by a scraper.

DEHYDRATION OF THE PULP.

The removal of water, as far as possible, from the pulp is an important operation, especially if the pulp is to be shipped, because the smaller the content of water the less the expense for freight will be. If the pulp is to be used in the establishment itself in which it is prepared, thorough dehydration is of course not required, it being only necessary to free it from water sufficiently to allow of the preparation of boards, in which state it is further worked, the finished boards being finally completely dried.

The board machine consists in the main of an endless cloth 10 to 13 feet long which is stretched tight over rolls so as to present a perfectly level surface. Over this cloth, several wooden rolls lie loose in crotches, their object being to distribute uniformly the quite thinly-fluid pulp taken up by the endless cloth and, at the same time, to somewhat squeeze it out by their weight. By this means quite a tenacious paste is obtained on the portion of the endless cloth opposite to where the pulp enters. This paste is then pressed more vigorously between two iron rolls so that it forms a quite firm, coherent mass. This is allowed to wind several times round a roll and the hollow cylinder thus formed is cut through, all the sheets thus produced being of the same size. Sheets of any desired length may also be formed upon an endless cloth which takes up the pulp. If, however, in place of sheets thoroughly dried, or more correctly, thoroughly dehydrated, pulp is to be produced, the pulp is allowed to flow over a cylinder covered with wire cloth, both ends of which are rendered as tight as possible by rubber, and under which vigorous rarefaction of air is maintained. The pulp flowing upon the slowly

revolving sieve is much dehydrated by the air-pressure and is removed in the form of a coherent mass. It is then again vigorously pressed between rolls and finally divided by smooth rolls into small pieces which are immediately packed.

If, however, the pulp is to be freed as much as possible from water as would seem necessary for transporting it long distances, filter-presses are used, a quite powerful hydrostatic pressure being produced by means of an accumulator. In the chambers of the press, sheets quite dry to the touch are thus obtained, which can be readily packed and transported long distances. The only drawback as regards the use of filtering-presses is that a plant working on a larger scale would require a number of them to work up rapidly all the raw material furnished by the grinding machine.

DRYING APPARATUS.

The preparation of perfectly dry pulp has recently been successfully accomplished without too large an expenditure, by the use of apparatus which in its construction closely resembles the contrivances employed in sugar houses and breweries for drying beet slices and grains. They are so arranged that the substance to be dried moves in a direction opposite to that of a hot air current, so that drying is effected by a counter-current. The substance to be dried is first met by the hot air-current while it still contains all the water, and though it becomes highly heated, it loses but little water by evaporation, the latter process, however, proceeding very rapidly as the heated mass advances.

The apparatuses used for drying pulp are generally so arranged that the crumbled pulp previously freed as much as possible from water by mechanical means, is carried along with a certain velocity upon endless wire cloth, while underneath the latter a hot air-current passes in an opposite direction. The velocity of the movement of the pulp upon the cloth is fixed by the temperature, and the latter has to

be carefully regulated. By the use of such an apparatus the pulp may be only partially or completely dried, as may be desired. The apparatus is furnished with automatic charging and discharging contrivances.

PROPERTIES OF WOOD-PULP.

With the exception of pulp completely freed from water by artificial drying—and this exception applies only to material dried shortly after its preparation—its color undergoes a considerable change, which, of course, is also transmitted to the paper prepared from it. Experiments made by Cl. Winkler with pulp from different varieties of wood which was exposed to the action of the air at a temperature of between 30° and 50° F., gave the following results:

COLOR OF PULP.

From	*When freshly prepared*	*After several weeks.*
Pine	pale yellow	pale yellow
Fir	yellow	yellow
Scotch fir	greenish-white	dirty reddish
Larch	pale yellow	pale yellow
Aspen	yellowish-white	yellowish-white
Linden	gray-white	gray-white
Maple	yellowish-white	yellowish-white
Beech	pea yellow	superficially reddish
Birch	yellowish-white	flesh color
Alder	deep yellow	brick-red

The change of color appears first upon the surface of the moist pulp, spreading from there to the interior, and is, without doubt, a process of oxidation. Since pure cellulose does not exhibit this change of color, it can only be caused by a chemical change of the lignin and eventually of the very small quantity of protein substances. The content of rosin in the conifers appears to exert but little influence as regards the change of color, as will be seen from the behavior of the pulp prepared from them.

The change in color of the pulp being very annoying as regards the paper made from the material, experiments

have been made to overcome this defect by bleaching. Of all the bleaching agents experimented with, sulphurous acid, produced by burning sulphur, is the only one which has proved of value in practice. The simplest mode of application is to conduct sulphurous acid into an air-tight box which is filled with broken pulp containing 60 per cent. of water. The gas is absorbed with avidity by the water, and the entire mass is in a short time saturated with it. Pulp thus bleached should not be allowed to lie too long, since it has been shown that after some time it contains sulphuric, in place of sulphurous, acid. When the pulp is dried in the air, the sulphuric acid acquires a certain concentration and has a browning effect upon the pulp. Hence the bleached mass should immediately be worked further.

The effect of the sulphurous acid appears to be that, on the one hand, it arrests the oxidizing action of the air, and, on the other, that it enters with the coloring matter contained in the pulp into a colorless combination, which, however, is in the course of time again decomposed, the sulphurous acid being again liberated and slowly oxidized to sulphuric acid.

PULP FROM STEAMED WOOD.

When treated with water under high pressure and at a high temperature even pure cellulose is chemically changed and converted into hydrocellulose. Wood, when treated in a similar manner, undergoes, however, more far-reaching changes, the lignin contained in it being very likely most effected, because by the treatment with high-pressure steam the fibres are considerably loosened, and there is no difficulty whatever in preparing from such wood a pulp which is distinguished by particularly long fibres.

The quantities of substances which pass into solution by steaming vary according to the variety of wood. In steaming beech 26.75 per cent. passes into solution, 11.19 per

cent. of this being sugar and substances resembling sugar. Steamed pine showed a loss in weignt of 19.17 per cent., 9.07 per cent. of this being sugar and substances allied to it. The latter probably consist chiefly of dextrin-like bodies, since the wood extract yields with alcohol very heavy precipitates.

However, in addition to the bodies mentioned above, there are formed in steaming wood, combinations like those appearing in abundance at the commencement of the destructive distillation of wood. In water in which wood has been steamed are found considerable quantities of acetic and formic acids. When resinous woods are subjected to steaming, considerable quantities of volatile oil escape with the aqueous vapor when the pressure in the vessel used for steaming is interrupted.

By steaming the wood acquires a more or less dark leather to liver-brown color, and the fibres are very much loosened. By reason of this brown coloration of the wood, the pulp prepared from it cannot be used as an addition in the manufacture of white paper. It is, however, very suitable for the production of stout wrapping paper, because it has very long fibres, which, in making it into paper, felt together, the resulting product being very durable and flexible.

In its construction the apparatus used for steaming wood resembles a cylindrical steam boiler, both upright and horizontal types being used. It is advisable to line the walls of iron boilers with copper, they being in the course of time strongly attacked by the organic acids formed from the wood.

The production of pulp from steamed wood may be effected in various ways. When working with the ordinary grinding apparatus, the wood is prepared in exactly the same manner as the ordinary material, *i. e.*, it is freed from bark, the knots are cut out, and the blocks are finally cut into lengths to fit the pockets of the machine,

and split. The blocks are then brought into the boiler and for 8 to 12 hours treated with steam of 4 to 6 atmospheres. The higher the tension of the steam and the longer the wood is exposed to it, the more energetic its action upon the encrusting substance and the darker the color of the wood will be.

On subjecting steamed wood to a microscopical examination, it will be found that the greater portion of the encrusting substance has disappeared and that the vascular bundles consisting of cellulose are quite uncovered. By long-continued steaming under high pressure, it might be possible to bring all the encrusting substance into solution, and thus obtain a product which does not essentially differ from pure cellulose. However, in practice, this process cannot be profitably applied because, on the one hand, by long-continued steaming under high pressure, a portion of the cellulose itself is hydrolized, causing a considerable reduction in the yield, and on the other, the cost of production is much increased. Hence steaming is continued only long enough for the wood to acquire a sufficient degree of softness, when it is submitted to the grinding machine. In grinding steamed wood much less power is required than in working the raw material, which is readily explained by the breaking-up of the coherence of the vascular bundles by steaming.

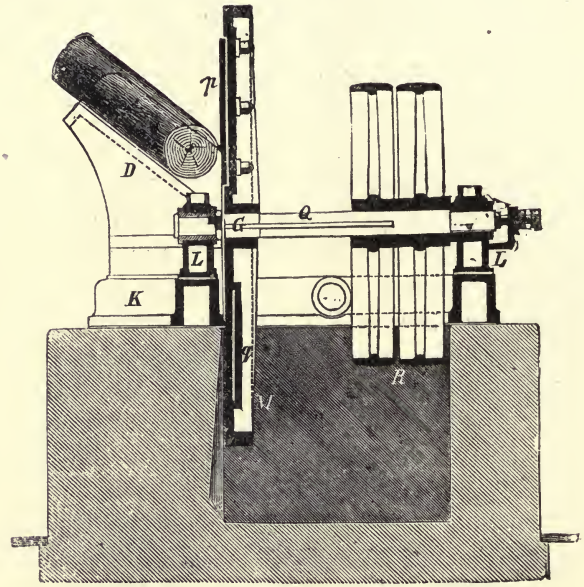
PREPARATION OF MECHANICAL WOOD-PULP BY THE CRUSHING PROCESS.

A process—called by the inventor the *crushing process*—for the preparation of pulp from steamed wood without the necessity of grinding, has been invented by Rasch-Kirchner of Frankfort-on-the-Main.

The steamed wood to be worked is first converted into small pieces by means of a chopping machine of original construction, the arrangement of which is shown in Figs. 19, 20, and 21. In a strong iron frame, *K*, rests in the

bearing, *L*, the shaft, *A*, which carries a heavy disk-knife, *M*. The latter in revolving passes the box, *D*, and by means of the knife, *p*, cuts the wood only lengthways into shavings of fixed size, or lengthways as well as crossways, if the cross-slitters, *o*, are at the same time applied. The construction of the machine is such as to allow of its being set so that the wood can be cut up in different ways. The wood may be placed in an oblique position and the cross-

FIG. 19.

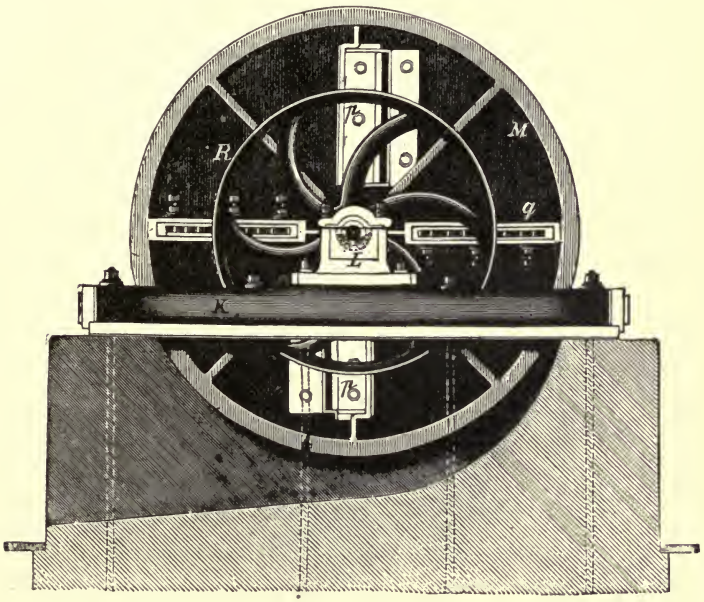


sections thus obtained can readily be reduced to pieces. By placing the wood so that it is worked perpendicularly to its length and bringing the knives which serve for the production of cross-slits into activity, shavings 1¾ inches wide and long and from 0.11 to 0.19 inch thick may be obtained.

The small pieces of wood coming from the machine are then still further reduced by mechanical means, they being

first subjected to the action of a stamping mill in which they are reduced to such a degree that they can be transferred to the hollander, a machine used in paper mills for the disintegration of paper-stuff. In this apparatus the mass may be worked till it has become sufficiently uniform for the direct preparation of boards in the board machine. If, however, loose pulp is to be produced, the sorters em-

FIG. 20.



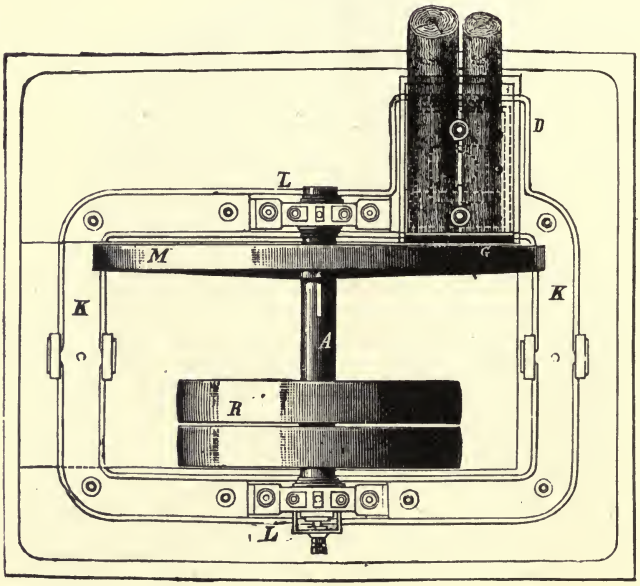
ployed for ground wood have to be used in order to separate the coarser particles from the finer fibres.

However, the course most generally pursued in working the mass obtained from steamed wood, is to manufacture from it at once brown boards or stout wrapping paper. A pulp with longer fibres being more readily obtained from steamed wood than from wood not steamed, boards and paper made from it possess greater strength, the boards being especially suitable for roofing purposes. Roofs cov-

ered with such boards properly impregnated with coal-tar possess great capability of resisting the action of the weather, being perfectly indifferent to water as well as to changes in temperature.

Numerous attempts have been made to bleach the pulp from steamed wood, but thus far without satisfactory results, no effect worth speaking of being produced on it even by the most powerful bleaching agents. It is very likely

FIG. 21.



that the coloring bodies formed in steaming wood belong to the group of combinations to which the term humus bodies has been applied. They are distinguished by a very dark brown to black color which it is impossible to lighten up by any bleaching agent.

Physically, ground wood actually differs from the original material only in that the individual vascular bundles appear to be quite completely separated one from the other.

However, the individual vessels adhering together are still firmly connected by the encrusting substance—the lignin—this fact being shown by storing the pulp for some time exposed to the light, it acquiring in a short time a quite strong brownish coloration. This coloration also appears in the paper-mass to which the pulp has been added. Paper thus prepared turns perceptibly brown when for a few weeks exposed to the light, and at the same time becomes brittle. The manufacture of paper which could lay claim to durability for a longer time would therefore appear impossible with the use of larger quantities of mechanical wood-pulp, it being possible only when pure cellulose, the great stability of which has previously been referred to, is employed.

III.

PREPARATION OF CELLULOSE FROM WOOD. (WOOD-CELLULOSE, CELLULOSE IN THE TECHNICAL SENSE OF THE WORD, CHEMICAL WOOD-PULP.)

Paper consists of cellulose fibres felted together in a peculiar manner so that the individual fibres can no longer be distinguished. The cellulose which was formerly exclusively used for the manufacture of paper consisted of waste of linen and cotton fabrics, and other vegetable fibrous substances. By reason of the constant increase in the consumption of paper, the price of this waste, technically called rags, rose steadily, so that the efforts of chemists were for a long time directed towards finding a substitute for rags in another vegetable substance. After many experiments, the results of which, however, were not very satisfactory, a process was finally discovered which allowed of the separation of cellulose from certain varieties of wood in such a form as to render it suitable for use in the manufacture of paper. The production of cellulose from wood has now become a highly developed industry, and every year the quantity of raw material worked up becomes larger.

In the preparation of cellulose from wood, the principal point is the removal of the substances which incrust the cellulose, and to convert the latter into actual wood substance, as well as to obtain it in a pure form. It is, however, also of importance that the individual fibres should be of a certain length to allow of them being properly felted together into paper, and the solution of this demand

presented for a long time many difficulties which, however, finally were successfully overcome.

There are quite a number of methods by which wood cellulose may be prepared, but only three of them—namely, the soda process, the sulphite process and the electric process—have at present been firmly established in practice. The sulphite process, while it yields the same favorable results, is far more simple in execution than the soda process, and is more and more replacing the latter, many wood-cellulose plants at present working exclusively with it.

Since the encrusting substance of the wood may also be destroyed by acids, a series of processes have from time to time been introduced, the object of which is to effect the disintegration of the wood-fibre by their use, concentrated nitric acid, as well as *aqua regia*—a mixture of nitric and hydrochloric acids—having been employed for the purpose. However, independent of the great expense connected with them, these processes have the further disadvantage that it seems next to impossible to keep the operating vessels tight, in consequence of which products of decomposition of nitric acid escape into the work-room, rendering the air of the latter very injurious to the health of the workmen. For these reasons, this method of preparing cellulose has been entirely abandoned. It may, however, be mentioned that one acid process by which the disintegration of the wood is effected with hydrochloric acid, would seem to be available, since it yields a very valuable by-product.

BACHET AND MACHARD'S METHOD.

According to this method thin slices of fir are subjected to hot treatment with hydrochloric acid. Four thousand eight hundred pounds of fir in thin slices are brought into a wooden vessel and after pouring over them 2000 gallons of water and 1760 lbs. of hydrochloric acid, the fluid is brought to boiling by the introduction of steam, boiling being continued for 12 hours. The fluid is then drawn off

and neutralized with calcium carbonate. It now represents a dilute solution of grape sugar which can be brought by yeast into vinous fermentation, and by distillation yields a considerable quantity of alcohol. The residue consisting of cellulose is washed with water until all the acid is removed, crushed under millstones and disintegrated in the hollander. Since by this process a considerable portion of the cost of manufacture is covered by the alcohol gained as a by-product, it would appear to be of importance for the practice. To judge, however, from its present state, this method has many inherent defects which prevent its general introduction. If, however, these defects can be overcome, it might prove of importance for the manufacture of cellulose. Later on more modern processes for obtaining alcohol from wood will be referred to.

PREPARATION OF CELLULOSE BY MEANS OF SODA.

This method of preparing cellulose is an American invention—poplar, pine, spruce, and occasionally birch, being used for the purpose. Poplar is especially distinguished from other woods in yielding very long-fibered cellulose. This process which may be called the American wood-pulp system can also be profitably applied to the conifers indigenous to Europe.

The first step in the manufacture is, in all cases, the mechanical preparation of the wood to be worked. This consists in carefully freeing the wood, cut up into short blocks from the bark, cutting out the knots by special machinery and reducing the blocks to chips about $\frac{3}{4}$ inch long, $\frac{1}{3}$ inch wide, and 0.19 to 0.31 inch thick. All the mechanical operations: Freeing from bark, cutting out knots, etc., are carried out by special machines.

The disintegration of the encrusting substance of the wood is effected by means of caustic soda lye. The statements regarding the quantities of soda lye—relatively of caustic soda—required for working 220 lbs. of wood vary

very much, but the quantity of caustic soda obtained from 48.4 lbs. of carbonate of soda is said to be sufficient in all cases. By the action of the caustic soda, the encrusting substance of the wood is destroyed and the resins are saponified. When the process of disintegration is finished, the fluid is discharged and evaporated in iron pans to dryness. The residue is heated in a reverberatory furnace whereby the acids fixed to the soda are destroyed, carbonate of soda remaining finally behind. This carbonate of soda is again converted into caustic soda, so that for the next operation only a sufficient quantity of fresh caustic soda to replace that unavoidably lost in the wash waters is required.

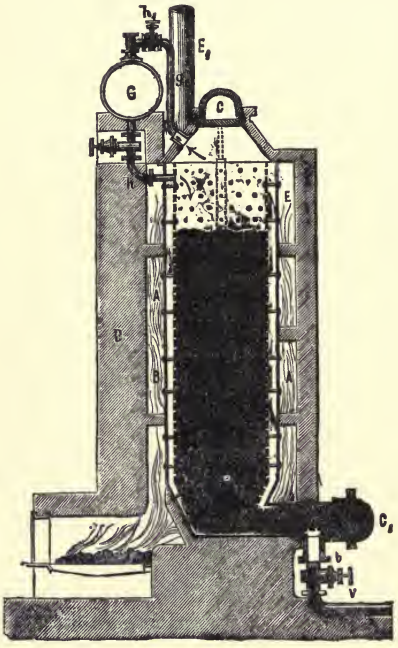
Sodium sulphite having the same destructive effect upon the encrusting substance as caustic soda, it is frequently substituted for a portion of the latter. This is effected by evaporating the lye which has once been used for boiling the wood, together with sodium sulphate, which is quite cheap, and heating the residue. By the carbonization of the organic combinations contained in the salt-mass, the sodium sulphate is reduced to sodium sulphite and a fluid is obtained which, when again made caustic, contains, in addition to caustic soda, a certain quantity of sodium sulphite.

To free the chips of wood from the encrusting substance by boiling them with soda lye in open vessels, would require so much time as to make the process scarcely available for practical purposes. If, however, the lye is allowed to act under increased pressure upon the wood, disintegration will be accomplished in a comparatively shorter time and with greater rapidity, the greater the pressure is and the higher the temperature prevailing in the apparatus. In practice a pressure from 6 to 14 atmospheres is used, though one from 10 to 11 atmospheres is most frequently employed.

SINCLAIR'S BOILER.

From what has been said above, the construction of the boiling apparatus must be such as to be capable of resisting the high pressure prevailing in its interior, as its explosion might cause terrible accidents. Since, considering the size of the boilers, even if constructed of the best quality of steel, it is difficult to keep them tight under the high pressure, of, say 14 atmospheres, prevailing in them, an ingenious contrivance to decrease the pressure is made use of in Sinclair's boiler, the actual boiler being enclosed by another boiler also made of steel. In the inner boiler in which the soda lye acts upon the wood, prevails a pressure of 14 atmospheres, while in the space between the inner and outer boilers circulates steam of 6 atmospheres, and hence the pressure upon the wall of the inner boiler is reduced to 8 atmospheres. The arrangement of Sinclair's boiler is shown in Fig. 22. The vertical boiler consists of a cylindrical vessel *A* tapering above and below. In this vessel stands a second one *B*, of the same form, which, however, is constructed of thin sheet iron, and its surface is perforated with holes. Its diameter is such that the walls of *B* are at a distance of 1.18 to 1.57 inch from *A*. *B* is the portion of the apparatus which serves for the reception of the wood. The boiler is charged through

FIG. 22.



the aperture C, and after the operation is finished, the fluid is discharged through the pipe C_1. The vessel G serves as a storage reservoir for soda lye and is so arranged as to allow of the introduction of lye into the boiler during the operation without a decrease in the pressure taking place. When lye is to be introduced, the lower cock h is first opened, and then the upper one h_1. The same pressure then prevails in the vessel G as in the boiler and lye may run into the latter. The entire apparatus is heated by an open fire from the fire-place F. The lower portion of the boiler is protected by brickwork to prevent its coming in direct contact with the flame. The flames pass upwards through special flues which are so arranged that the flames come on every side in contact with the boiler.

UNGERER'S BOILING PROCESS.

In some systems of boiling wood an entire battery of boiling vessels, one connected with the other, is used instead of a single boiler. When the boilers have been filled with wood, soda lye is introduced into the first one, and allowed to act upon the wood for some time, for instance, one hour. Fresh lye is then introduced into the first boiler in such a way that the fluid contained in it is forced into the second boiler. In about one hour fresh lye is again brought into the first boiler, the lye contained in the second boiler being forced into the third one, and so on. Hence the wood is constantly treated with fresh lye, and disintegration is effected more completely and in a shorter time than when the wood is always boiled with the same quantity of lye. The system sketched above has been introduced by Ungerer. In its arrangement the apparatus closely resembles the diffusion apparatuses used in sugar houses and in factories for the preparation of dye extracts. It seems probable that by this method the object of the disintegration of the wood might be accomplished with certainty and in the shortest time.

KEEGAN'S PROCESS.

This process for the disintegration of the wood by means of caustic soda, differs essentially from the methods in which the wood is heated under high pressure with soda lye. The process in its distinctive features consists in that the wood is brought into a vessel from which the air is exhausted. The cold soda lye is then introduced and the pressure upon the fluid raised to 3½ atmospheres. When it is supposed that the wood is completely saturated with soda lye, the lye not absorbed is allowed to run off and the vessel is heated to 302° F. The quantity of soda lye absorbed by the vessels of the wood suffices to bring into solution all the encrusting substances, and one great advantage of this process is that the wood treated with lye need only be washed with a small quantity of water in order to regain from it the greater portion of the soda. Hence only a comparatively small quantity of fluid has to be evaporated, thus saving considerable in operating expenses, since the great consumption of fuel conditional to the evaporation of a large quantity of lye is one of the drawbacks of the process of producing cellulose by means of caustic soda.

The mass of wood boiled according to one of the methods above described, consists of cellulose, the interspaces of which are filled with the fluid which has been formed from the soda lye and the substances absorbed by it. The next problem is to obtain this fluid as completely as possible, so that the soda contained in it may again be brought into use. However, so as not to use too much fuel for evaporating the lye, the recovery of the soda should at the same time be effected in such a manner that as little fluid as possible is obtained. In order to attain this object as completely as possible, the system of gradual lixiviation employed everywhere in chemical establishments when a solid body has to be entirely freed from adhering fluid, is made use of in cellulose plants.

In working according to this method a battery has to be used in which lixiviation is effected by means of a current. The distinctive features of such an apparatus are as follows: A number of vessels—ten to twelve—are connected one with the other in such a way that when the level of the fluid in the first vessel reaches a certain height, the fluid running off rises from the bottom through a pipe and can flow into the next vessel. When these vessels are filled with the mass coming from the boiler and water is poured into the first vessel, it will in a short time become mixed with the fluid contained in the mass of wood. By now allowing more water to run into the vessel, the fluid contained in it is forced into the next vessel where it becomes more enriched with soda. Now, with the use of twelve lixiviating vessels, the mass in the first vessel will have been twelve times in contact with water at the time when the last vessel has just been filled. When water is then again poured into the first vessel, a corresponding quantity of fluid will run off from the twelfth vessel. This fluid is a very saturated soda solution, and the quantity of soda contained in it corresponds with that present in the fluid discharged from the boiler. The mass of cellulose in the first vessel is now completely washed and can be immediately subjected to further working by mechanical means.

While the first vessel is being emptied, the course of the supply of water is so changed that the second vessel of the battery becomes the first and in this manner lixiviation is systematically continued.

A number of contrivances, such as counter-current washing machines, wash-drums, etc., have been introduced for washing cellulose, which do good service provided they fulfill the object of lixiviating the cellulose mass in the most complete manner, and with the smallest possible consumption of water.

PREPARATION OF CELLULOSE BY MEANS OF SODIUM SULPHITE.

It has been previously mentioned that in preparing cellulose with caustic soda a portion of the latter may be replaced by sodium sulphate. This salt, to be sure, does not take part in the process, but when the used lyes are evaporated and the residue is heated, it is converted into sodium sulphite, which, like caustic soda, has a destructive effect upon the encrusting substance of the wood. Hence, in the course of the operation, before evaporating the used lyes, it is only necessary to add to them a determined quantity of sodium sulphate in order to obtain by the regeneration of the salt, the corresponding quantity of sodium sulphite. The highly evaporated lyes are mixed with limestone and coal-dust, and after drying, melted in a reverberatory furnace, whereby caustic soda and sodium sulphite are obtained. After washing the salts with water, they are dissolved and used for boiling. For every 100 parts of dry substance of the lye used, 100 parts of limestone and 25 parts of coal-dust are used.

The further working of the washed cellulose is effected by purely mechanical means. As a rule, the pieces of cellulose, which still retain largely the form of the fragments of wood originally used, are ground in a mill with water to a paste. This paste is mixed with a large quantity of water and made homogeneous in the hollander. If to be used in the manufacture of finer qualities of paper it is also bleached with chlorine. The value of cellulose is the greater the longer its individual fibres are, because long fibres felt more completely together than short ones, the resulting paper being much stronger. However, generally speaking, finer qualities of paper are not made from wood cellulose alone, the pulp for them consisting, as a rule, of cellulose prepared from rags mixed with a certain percentage of wood-cellulose.

The statements regarding the consumption of wood and chemicals in the different factories vary so much as to render it difficult to give a correct idea of it. Moreover, the yield of cellulose appears to be essentially effected by the content of water in the wood to be worked. The content of water in thoroughly air-dry wood is about 20 per cent., while in many varieties of wood, when freshly cut, it may amount to twice as much, and for that reason the yield of cellulose will turn out quite different from that calculated from the weight of the wood. The nature of the wood to be worked is also of great influence upon the yield of finished cellulose, as shown by the following figures given by Reid :

Variety of wood.	*Cellulose in per cent.*	*Length of fibre.*
Beech	38.5	short
Birch	42.0	short
Hemlock spruce	37.5	long
Poplar	41.7	medium
Pine	39.0	long
Fir	38.0	long.

PREPARATION OF CELLULOSE WITH THE ASSISTANCE OF SULPHITES. (SULPHITE–CELLULOSE ACCORDING TO MITSCHERLICH'S PROCESS).

Solutions of acid sulphites possess, similar to caustic alkalies and their combinations with sulphur, the property of dissolving and destroying the encrusting substance of wood. The process of preparing cellulose in this manner is the invention of the German chemist Mitscherlich, all other sulphite processes being more or less suitable modifications of it. In establishing a sulphite-cellulose plant it is of the utmost importance that an abundance of water should be available, and besides the conditions must be such that the waste liquor can be discharged into a water-course of considerable size. For the manufacture of 4,400 lbs. of air-dry cellulose about 15,000 gallons of water are required, and the waste liquor of the plant must be diluted to such an

extent as not to be detrimental to the existence of animals in the streams into which it is discharged, since otherwise the unavoidable consequence would be that the plant would constantly have to pay large amounts for damages to the proprietors of the fishing rights in the respective streams, and might even be forced entirely to suspend operations.

The wood has to be prepared with special care and should be used as soon as possible after having been cut down. In case wood which has been cut for some time is to be worked, it should previously be for a few days placed in water. Since there is a difference in the behavior of the various kinds of wood toward the sulphites, only one special variety should at one operation be worked.

The trunks to be used must be carefully freed from bark and bast, and adhering dirt is to be removed, so that only perfectly clean wood is brought into the saw-mill. In the latter, the trunks are cut by circular saws into blocks about 16 inches long, and the knots cut out by a suitable machine. Finally the blocks are cut up into thin discs not more than 1 inch thick, which are again inspected, pieces with knots in them being rejected. In preparing the wood in the manner above described there will naturally be considerable waste, and besides a large quantity of sawdust. The latter, to be sure, can be worked together with the discs, but readily causes annoyance and trouble by obstructing pipes, etc. Hence, in many plants the practice of cutting the blocks into discs has been entirely abandoned, the blocks being converted by a machine resembling a planing machine, into thin boards 0.27 to 0.29 inch thick, an essential advantage of this procedure being that the longitudinal fibres of the wood are preserved and cellulose of greater length can be obtained.

Pine is considered the best material for the preparation of sulphite cellulose, and next to it, fir is most highly valued. Scotch fir, to be sure, is also suitable for the pur-

pose, but only the sap-wood should be used, the heart yielding cellulose of a dark color. Other varieties of wood, including deciduous trees, may also be used, but the cellulose obtained from them is not as strong as that from conifers, and the yield of finished cellulose is small.

The preparation of cellulose by the sulphite process may be divided into three principal operations:

I. Preparation of the sulphite solution.
II. Boiling the prepared wood with the solution.
III. Treatment of the cellulose mass obtained.

PREPARATION OF THE SULPHITE SOLUTION.

According to Mitscherlich's process, the incrusting substance of the wood is dissolved by the use of solution of calcium bisulphite, obtained by treating calcium carbonate with sulphurous acid. The operation is carried out as follows:

Sulphurous acid in gaseous form is conducted into a vessel filled with porous limestone, water being at the same time allowed to flow over the limestone. From the limestone, from which the carbonic acid has been expelled, neutral calcium sulphite is first formed. However, since sulphurous acid is present in excess, it ascends in the vessel, dissolves in the water trickling down and flows back over the neutral calcium sulphite, which, as it dissolves with greater difficulty than the limestone, has settled upon the latter. Calcium bisulphite, which dissolves with ease, is now formed, and the resulting solution of this salt runs off into a collecting reservoir. In cellulose plants this solution is briefly called *lye*, and by this term it will be referred to throughout the succeeding pages.

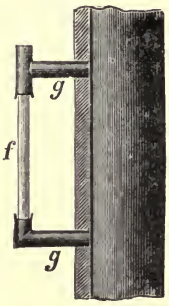
Very large quantities of lye being required in a cellulose plant, the apparatus for its preparation must be of adequate size. In reference to this, Mitscherlich, who has worked out to the smallest details the entire operation of this process, makes the following important statements:

The limestone serving for the preparation of the lye should be as pure as possible, so that not too much mud is formed by foreign substances (magnesia or organic substance) contained in it. It should further be very porous and at the same time firm, so as not to be crushed by the weight of the layer over it, which might cause troublesome obstructions in the apparatus. A material which can be recommended for the purpose is solid tufaceous limestone in pieces about the size of the fist, which are piled up to the height of 39.37 inches in the tower-like structure in which the lye is prepared. To prevent the pieces of limestone from packing too closely together and crumbling in falling down the entire height of the tower, the latter is filled to a certain depth, and a fresh charge equal in size to the original one is introduced from the top of the tower when the layer of limestone has sunk to a certain depth.

The sulphurous acid required for the preparation of the lye is obtained by burning sulphur or, if cheaper, pyrites. Sulphur-burning is an operation requiring careful regulation, so that combustion is complete and no unburnt sulphur reaches the absorbing tower. One of the best tests in this respect is the color of the flame, which should be pure blue. The appearance of a yellow, dark flame is an indication of an insufficient admission of oxygen, the consequence of which is generally an evaporation of unburnt sulphur which may damage the pipes and become very troublesome. Incomplete combustion of the sulphur may be due to an inadequate supply of air to the furnace itself, but it may also be caused by the current of gas ascending in the absorbing tower not being strong enough, and hence the entire apparatus needs careful watching. In order to have, in addition to the appearance of the flame, a means of testing whether sulphur in the form of vapor is carried along with the sulphurous acid, a wide glass tube, *f*, Fig. 23, is inserted in the pipe through which the sulphurous acid is conducted, a portion of the latter passing through

the glass tube, and the appearance of a yellow tinge in the latter is an indication of a content of unburnt sulphur in the gas. The arrangement of the absorbing tower in which the formation of the lye takes place is shown in Figs. 24 and 25. The pipe through which the sulphurous acid is conducted from the furnace *k* should rise at least two-thirds the height of the tower, then turn downward at a right angle and enter the tower from below. The ascending portion *a* of this pipe is constructed of iron, while the descending portion *b* consists generally of tile-pipe. The nearly horizontal portion of the pipe through which the gas enters the tower must by all means consist of tile-pipe. The diameter of the pipe should be such that the gases are not exposed to considerable friction and may sufficiently cool off before entering the tower.

Fig. 23.



The absorbing tower is 105 feet high and about 5 feet square. It is constructed of wood, very resinous wood, for instance, Scotch fir or pitch pine, being used. Larch being expensive is more seldom employed. The walls of the tower must be thick, the lower portion being made 3.15 inches, the centre portion 2.36 inches and the upper portion 1.57 inches thick. The separate parts of wood are held together by stout iron hoops secured by screws, they, as well as the screws, being carefully coated with tar. Joints between the parts of wood are stuffed with tow and coated with tar.

The lower portion of the tower is furnished with a grate *h* of oak beams, which must be strong enough to support the load of the layer of limestone placed upon it. Between the grate beams are openings 2.95 inches wide through which the gases ascend and the lye runs down. The upper faces of the beams are 2.95 inches wide, but the lower ones only 1.96 inches. Two oak beams are also placed in the tower

3¼ feet above the grate for the purpose of partially relieving the latter. Boards placed horizontally are secured by

Fig. 24.

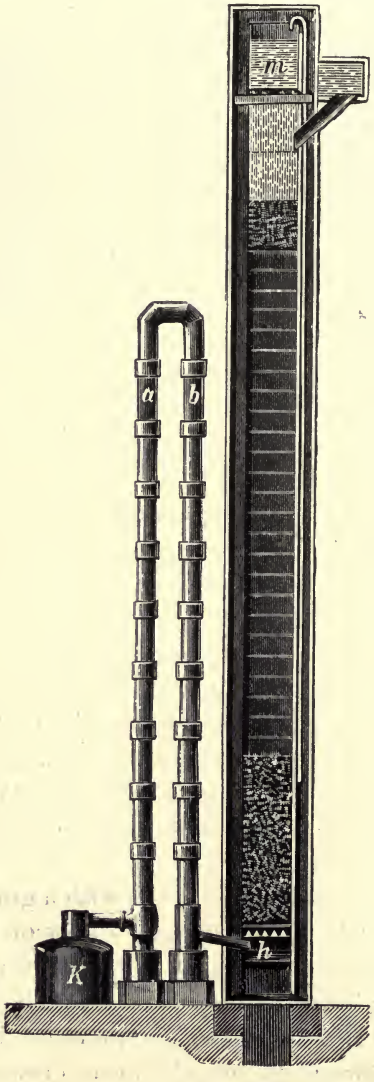
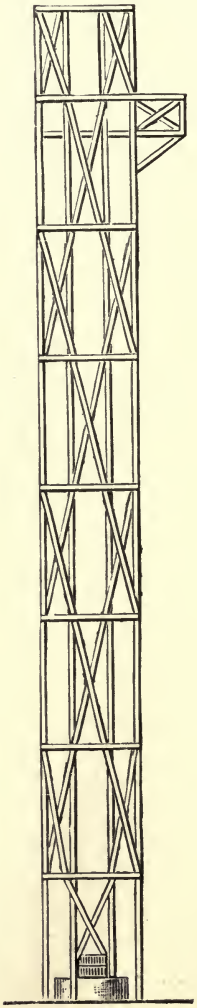


Fig. 25.



means of stout wooden pegs to the walls of the tower at

distances of 3¼ feet one above the other. These boards slope inward, so that the fluid dripping down upon them is conducted towards the interior of the tower and the walls of the latter are not moistened. Figs. 26 and 27 show on an enlarged scale the shape of these boards and the manner of fastening them.

Large as such a tower is, it is scarcely of sufficient size to prepare in it the lye required for one boiler. In order to carry on operations without interruption and to be able occasionally to clean a tower which has been in use for a

FIG. 26.

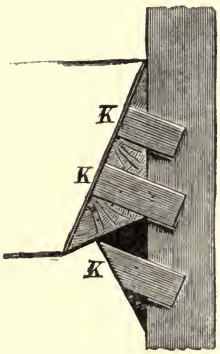
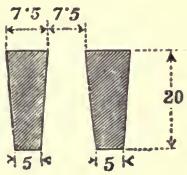


FIG. 27.



longer time, it would seem to be advisable to build four towers, erecting one on each corner of a square, and placing the stairs, water pipe and hoist for the limestone in the square. Reservoirs for the reception of the lye which is discharged through a lead pipe from the tower are located alongside the latter. The lead pipe is placed slightly above the bottom of the tower and is bent at a very obtuse angle like a siphon, thus forming a hydraulic joint which allows of the lye running off, but prevents the escape of gas from the tower. The lye first passes through the lead pipe into a barrel open at the top and divided into two compartments by a partition reaching half-way up. The greater portion of the mud carried along by the fluid settles on the bottom

of the barrel. From the bottom of this barrel the fluid passes through a lead pipe into another barrel filled with small pieces of limestone in which the small quantity of free sulphurous acid, which may still be contained in the lye, is fixed. After passing through this barrel, the lye runs into the actual lye-reservoirs.

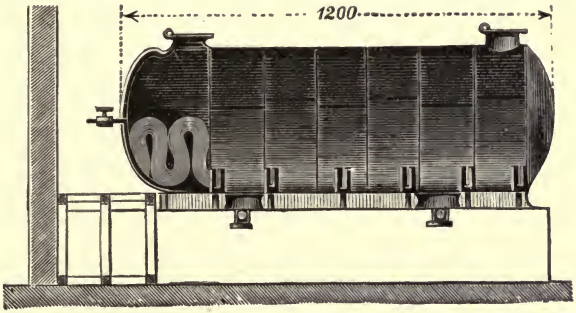
Large, prismatic, wooden boxes, 16⅔ feet wide, 10 feet deep and 23 feet long, serve for lye reservoirs, at least two of which should be provided for every boiler. The lye contained in one of these reservoirs being just sufficient for one boiling, the two reservoirs are connected by a wooden pipe so arranged that the connection can be cut off for the purpose of cleaning one reservoir while the latter is being filled. The conduits leading from the reservoirs to the boiler are also constructed of tarred wood, this material being more capable of resisting the action of the lye than all others, even not excepting lead.

In preparing the lye care must be taken that the sulphurous acid obtained by combustion reaches the tower entirely cooled off. When the odor of sulphurous acid commences to be perceptible at the upper aperture of the tower, water is introduced from the reservoir *m* placed at a higher level, and the supply is so regulated that the odor of sulphurous acid can just be noticed, the object in view, namely, to obtain a lye as concentrated as possible being in this manner most assuredly attained. In case an irregularity should occur in the course of the operation, it is either due to the sulphurous acid carrying along with it vapors of sulphur, or the supply of water is too small, so that the neutral calcium sulphite formed upon the pieces of limestone cannot be converted into the readily-soluble acid combination, or, finally, it may be caused by the current of gas being obstructed in the tower. In this case a remedy must at once be applied and an effort be made to overcome the disturbance by a stronger supply of water kept up for some time.

BOILING THE WOOD WITH THE LYE.

The object of this operation is to bring into solution the encrusting substance and convert the wood into cellulose. For this purpose a large iron vessel or boiler of cylindrical shape, Figs. 28 and 29, is used, which is furnished with four manholes, two on top and two on the bottom. All the fixtures for the introduction of lye, steam, etc., are placed on the lids of the manholes, because they can be more readily kept tight there than in any other place. To prevent the lye from coming in direct contact with the iron, the latter being strongly attacked by it, the interior surface of the boiler is first coated with a mixture of pitch and common tar, the proportions of the mixture being such

FIG. 28.



that, when heated the coat is quite thinly-fluid, but very sticky at the ordinary temperature. Upon this coat is laid a thin layer of sheet-lead, at least 0.07 inch thick, and rubbed down smoothly so that the interior surface of the boiler appears to be lined with lead. The portions of the boiler which have to be moved—the lids of the manholes, etc.—are provided with a double protecting covering of thicker sheet-lead. The interior space of the boiler is lined with brickwork as shown in Fig. 30. The brick used for the purpose should not be porous but of a porcelain-like nature. The lower portion of the interior surface of the

boiler is furnished with a double-brick lining, that in the upper portion being single. For the sake of a close joint, the bricks are grooved and tongued and the spaces between them filled with cement. Lining has to be done with the

Fig. 29.

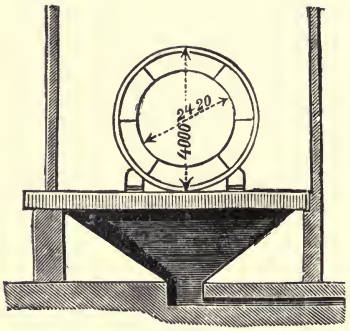
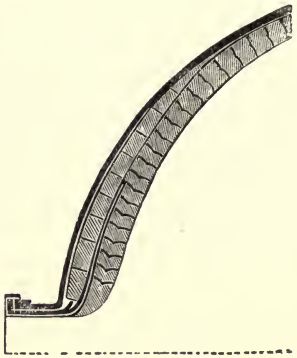


Fig. 30.



greatest care, and when testing the boiler in the cold up to six atmospheres no exudation of fluid should anywhere be perceptible.

Heating of the mass in the boiler is effected by four systems of heating pipes—see Fig. 28, below to the left. The heating pipes are made of hard lead—an alloy of lead and antimony—and they have comparatively thick walls—3.15 to 3.18 inches. For a boiler 39 feet long and 13 feet in diameter, the pipes of each heating system must have a length of 656 feet, hence a total length of 2,624 feet is required. The heating pipes are connected with the steam pipes and, on the places where they branch off from the latter, are provided with valves which prevent the lye from running into the boiler in case one of the pipes becomes defective.

The proportion between wood and lye is as follows: The lye should have a concentration of 7° Bé., and for every 70.62 cubic feet of boiler space 35.31 cubic feet of pine wood, together with the sawdust belonging to it, are used.

If weaker lyes are employed, the quantity of wood has to be correspondingly decreased; thus, for instance, with lye of 6°, one-seventh less the quantity of wood is taken. The wood and sawdust are as uniformly as possible distributed in the boiler, the latter being filled one-quarter full of wood, and the sawdust is distributed in piles upon the wood.

When the boiler has been filled with wood, the lids of the manholes are placed in position and their joints luted with a thick cellulose paste. The safety-valve is then relieved and the valves on the lower portion of the boiler are slightly opened. Steam is then introduced into the boiler in such a way that a very slight jet of it passes out of the lower valves, the object of this operation being to moisten the wood uniformly and to expel the air from its pores. In working dry wood, the steam is allowed to pass through the boiler up to ten hours, but for wood freshly cut and containing even considerable moisture, a much shorter time is required. When, after steaming is finished, the cold lye is allowed to run into the boiler, the steam in the pores of the wood is condensed and the lye penetrates quickly into the interior of the blocks of wood.

Immediately after the introduction of steam has been interrupted and the valves have been closed, the valve connecting the boiler with the lye reservoir is opened, and in consequence of the vacuum thus created in the boiler the lye runs rapidly into the latter. Steam is now continuously introduced through the system of heating pipes, so that the contents of the boiler are as rapidly as possible brought to a temperature of 230° F., this temperature being maintained as uniformly as possible for twelve hours, when it is gradually raised to 242.6° F.

When the temperature has reached 230° F. a series of tests are made to see how much effective calcium bisulphite is still present. The test is executed as follows: A glass tube about 7¾ inches long is suspended to a vertical stand which is furnished with marks indicating $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$ of the

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volume content of the glass tube. Ammonia is now introduced into the glass tube up to the $\frac{1}{32}$ mark, and the tube is then almost entirely filled with hot lye drawn from the boiler. The glass tube is then closed and ammonia and lye mixed by vigorous shaking. The glass tube is then suspended to the stand and in a few minutes a precipitate is formed, the semi-fixed sulphurous acid being neutralized by the ammonia, while calcium sulphite, which is soluble with difficulty, is separated as a precipitate. From the precipitate the proportion of the effective solution can be readily determined. When the precipitate is only equal to one-sixteenth of the length of the glass tube, boiling is nearly complete. When the precipitate is only equal to one-thirty-second, heating is immediately interrupted and the boiler emptied. A very rapid decrease in the precipitate towards the end of boiling is an indication of detrimental processes taking place in the boiler. When the lye in consequence of having been improperly prepared contains polythionic acids, a modification of the process in the boiler takes place, the calcium sulphite being then decomposed and calcium sulphate (gypsum) and sulphur are separated upon the wood. The wood remains brown and hard, and is not completely converted into cellulose.

When the operation is properly conducted, boiling is finished in from 36 to 48 hours.

For the purpose of regaining the sulphurous acid, an abundance of which is still contained in the lye after the operation, the lye is allowed to enter a lead coil which lies in a cooling vat and terminates in one of the towers. In the lead coil the water which is saturated with sulphurous acid is condensed and collected by itself, while the sulphurous acid passes into the tower, to be again used for the preparation of lye.

WASHING THE CELLULOSE.

When boiling has been finished, the contents of the

boiler are emptied into a receptacle underneath the boiler, and after the cellulose-mass has settled to the bottom, the supernatant fluid is discharged into a watercourse, provided it is in a highly diluted state. If this, however, is not the case, the fluid has to be mixed with a quantity of milk of lime sufficient for the conversion of the calcium bisulphite and the free sulphurous acid still contained in it, into calcium sulphite, which settles on the bottom of the receptacle and may be again converted into calcium bisulphite by the introduction of sulphurous acid into the water poured over it.

When the boiler has been emptied it is rinsed out with water, and before starting a fresh operation, it is advisable to subject it to a thorough examination and to knock off with a wooden mallet any gypsum which may have deposited on the brick work.

The cellulose-mass coming from the boiler contains certain quantities of finely divided gypsum, fragments of neutral calcium sulphite, and besides is saturated with lye. To free it from these admixtures it is subjected to the action of a stamping mill, the operation being assisted by large quantities of water. The cellulose-mass is directly conveyed by a transporting contrivance from the boiler to a funnel from which it falls into the stamping trough, in which, mixed with the proper quantity of water, it is subjected to the action of the stamps. The latter are so set that they cannot fall entirely to the bottom of the trough, crushing the mass being thus prevented. From the stamping mill the pasty mass runs off through broad gutters which are provided with sand-catchers for keeping back sand, grains of gypsum, etc., the particles floating on the top being retained by a cleaner placed over the fluid. From the gutters the pulp reaches an inclined cylinder covered with a wire sieve. The water runs off through the meshes of the sieve, while the cellulose in the form of crumbs leaves the cylinder at the lower end and is quite completely freed from moisture by rolls.

DEFECTS OF CELLULOSE AND THEIR REMOVAL.

Owing to deviations from the proper process of working, the finished cellulose may show various defects which may partially be remedied. According to Mitscherlich the most important defects are as follows:

The cellulose instead of being pure white shows a yellowish or brownish color. The cause of this phenomenon is due to the fact that towards the end of boiling the required quantity of sodium bisulphite was no longer present. Such cellulose can be made quite white by bleaching with chlorine.

Some white pieces not converted into fibre may occur in the otherwise uniform mass, which is an indication of too much wood having been brought into the boiler. Such cellulose may very well be used for the manufacture of firm and strong paper, but must first be carefully rolled. However, such cellulose is less suitable for bleaching.

The occurrence of black particles in the mass is generally due to insufficient cleaning of the wood before it is cut up, and is caused by rotten pieces of bark which have been left on the wood. The black spots may also be due to particles of the belts, this being a defect which cannot be removed. Some kinds of cellulose contain small, soft bundles of fibre of a brownish color which may have been caused by the respective particles having become too hot in the boiler, or by incompletely freeing the wood from bast. These defects, as a rule, disappear completely by subjecting the cellulose to bleaching with chlorine.

The occurrence of larger brown bundles of fibre of considerable firmness is mostly due to a gross error committed in boiling, or to the fact that some of the stamps of the stamping-mill have come too near to the trough. With the use of the proper quantity of water and a right width of the slits in the splinter-catcher, these pieces should have been retained during washing.

With the microscope small, lustrous crystals may some-

times be noticed in the cellulose, this being proof of an insufficient quantity of water having been used in washing.

If the microscope shows the presence of small particles of an earthy appearance it is an indication of too little wood having been used in boiling, these particles consisting of neutral calcium sulphite. They can be most readily removed by an addition of hydrochloric acid to the wash-water, but cellulose thus treated requires a larger quantity of chlorine in bleaching. A change in color of the at first pure-white cellulose during washing is due to small quantities of iron which reach the mass chiefly through the wash-water and iron utensils. This iron may also be removed by acidulating the wash-water with hydrochloric acid.

The finished cellulose may either be immediately used for the manufacture of paper, or it may be freed from the larger portion of water by pressure. If, however, it is to be kept without undergoing a change, it has to be completely dried, as otherwise it becomes readily mildewed, especially when exposed to heat.

Other methods for the manufacture of cellulose by the sulphite process differ in details only from Mitscherlich's process above described, all being based upon the proposition that by boiling wood under an increased pressure with solution of calcium bisulphite the encrusting substance is dissolved and the mass need only be thoroughly washed to yield a material available for the manufacture of paper.

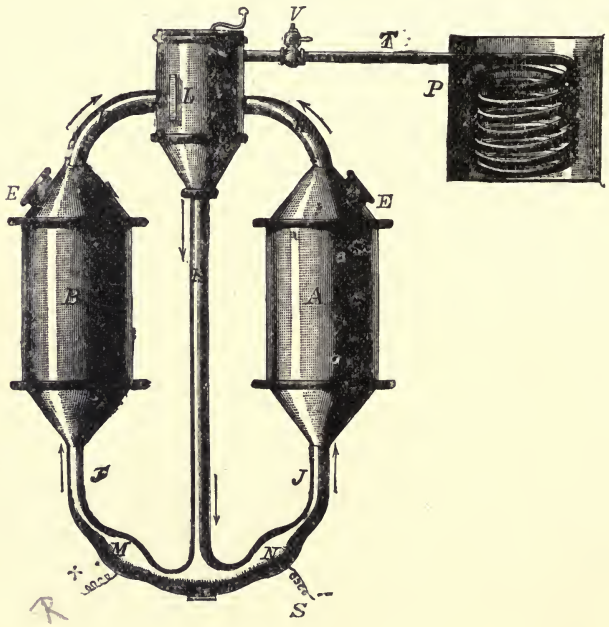
PREPARATION OF CELLULOSE WITH THE ASSISTANCE OF THE ELECTRIC CURRENT.—KELLNER'S PROCESS.

This process differs essentially from the methods previously described, and is based upon a very ingenious application of the electric current, the latter being used for decomposing common salt solution. When an electric current of suitable strength is allowed to act upon a solution of sodium chloride (common salt), caustic soda, free chlorine

and hypochlorous acid are formed. By allowing these bodies to act alternately at a suitable temperature upon wood, the lignin will in a certain time be completely destroyed and pure cellulose remain behind.

For carrying out his process, Kellner uses the apparatus, shown in Fig. 31, consisting of three boiling vessels *B*, *A* and *L*, which are connected one with the other by the pipes *H*, *J*, *M*, *N* and *K*, the positive pole of a source of electricity

FIG. 31.



(a dynamo) entering at *R* and the negative pole at *S*. When the apparatus is to be used, the boilers *A* and *B* are charged through the manholes *E* with wood prepared in the usual manner, and common salt solution is then allowed to run in until it becomes visible in the fluid-indicator *L* which is located in the intermediary boiler. Coils of pipe through which high-pressure steam is conducted lie in the boilers *A* and B. Heating is continued until the temperature of

the common salt solution has been brought to 262.4° F., when the electric current is closed, whereby the common salt solution is decomposed, caustic soda, free chlorine and hypochlorous acid being formed. The fluids containing these bodies ascend from *M* and *N* through *J J*, act upon the wood contained in *A* and *B*, and reunite in the vessel *L*. The gases accumulating in *L* are conducted through the valve *V* and the pipe *T* into the condenser *P*.

As will be seen from the above description, the wood in one of the boilers is treated with caustic soda lye and that in the other with chlorine and hypochlorous acid, both of these bodies having a destructive effect upon the encrusting substance. To make the process entirely uniform, the direction of the electric current is from time to time reversed, so that the wood which has been treated with caustic soda is exposed to the action of the chlorine and *vice versa*.

By reason of the powerful chemical action of the caustic soda and chlorine alternately exerted at short intervals upon the wood, the operation proceeds with greater rapidity and smoothness than by any other method, and cellulose in a perfectly bleached state is directly obtained from the apparatus. These advantages should certainly be sufficient to insure to Kellner's process extended application in practice.

PREPARATION OF CELLULOSE FROM STRAW.

While all efforts to prepare from the straw of our varieties of grain a cellulose suitable for the manufacture of finer qualities of paper were for a long time in vain, recent endeavors in this direction have been crowned with success, and this material is now worked on a large scale by several factories. In working straw for cellulose, the preparatory operations form a very important part of the process. The straw has not only to be freed from adhering earth, weeds, etc., but also as far as possible from the knots of the indi-

vidual stalks, these knots offering far greater resistance to the action of the chemicals than the tubular portions.

The operation is commenced by opening the bundles of straw and shaking out the weeds as much as possible. The straw is then cut very fine in a straw-cutter and cleaned by means of a fan. The current of air in the latter should be of such a force that the particles of stalks are positively carried away, while the heavier bodies, including the knot-pieces, fall to the bottom. If the operation is properly carried on, the greater portion of the knot-pieces, as well as the grain still contained in the straw, will be found in the mass collected in front of the fan, while the cut straw which has been blown away consists chiefly only of tubular particles of stalks.

For the further working of the winnowed straw the soda process is generally used, the encrusting substance of the straw being much more readily dissolved in the alkaline fluid than that of wood. Hence, boiling may be effected under considerably less pressure, three to, at the utmost five, atmospheres being in most cases sufficient.

The great volume occupied by the finely-cut straw is an objectionable feature which might necessitate the employment of boilers of very large dimensions. This may, however, be overcome by pressing down the straw in the boiler, while the lye is allowed to enter from below. By the action of the lye the bulk of the straw is very rapidly decreased and 1,100 pounds of straw can in this manner be readily worked at one time.

Horizontal cylindrical boilers of the revolving type have been found most suitable for working straw. The boiler having in the above-mentioned manner been filled with straw and lye, a portion of the latter is discharged, so that the boiler is only one-third full of lye. Steam is then introduced through the hollow trunnions of the boiler and the latter is made to revolve slowly—once in one or two minutes—around its axis. By boiling, the straw is con-

verted into a pasty mass, and boiling has to be continued until samples taken from the boiler show the complete disintegration of the knotty particles.

The boiler is then placed so that the man-hole is turned downward, and the pasty contents are allowed to run out. Since the individual particles adhere together in the form of fibres, the entire mass is passed through a stuff-mill consisting of a stationary bed-stone and a revolving runner.

Since the characteristic yellow coloring-matter of the straw is not decomposed by boiling with the alkali, the resulting cellulose would also be of a yellow color, and hence the mass has to be bleached. Before this is done, it must, however, be completely freed from alkali by washing, special apparatus being employed for this purpose.

Bleaching by means of chloride of lime is effected in the hollander, 11 to 22 pounds of chloride of lime being required for every 220 pounds of dry straw. During the process of bleaching, the mass must be kept in constant motion, and the operation should be effected at the ordinary temperature, since at an increased heat, the cellulose itself would be attacked by the chlorine and carbonic acid be evolved from the mass. The treatment with chloride of lime must be succeeded by thorough washing and, in case the finished product is not to be immediately used for the manufacture of paper, it has to be freed from water by hydraulic presses.

According to different statements, the yield of finished cellulose varies very much, but it appears to be chiefly dependent on the state of maturity of the straw used. From all that can be learned on the subject, a yield of 72.6 to 88 pounds of dry cellulose from every 220 pounds of straw used may be calculated on.

Besides the straw of the different varieties of grain, other parts of plants are utilized for the preparation of cellulose for the manufacture of paper, esparto (from *Stipa tenacissima*) especially being largely employed in England for that

purpose. The leaves of the esparto plant present the advantage of being very readily disintegrated, an increase in the pressure during boiling not even appearing necessary. The cellulose obtained from esparto is said to be distinguished by great firmness and pliability, so that it is suitable for the manufacture of very firm, white writing-papers. The quantitative yield also is said to be very satisfactory, 92.4 to 110 pounds of cellulose being obtained from 220 pounds of raw material.

Jute bagging, which has been used for shipping transatlantic products, is also utilized, when it can be had in sufficient quantities, for the preparation of cellulose, and this cellulose is especially suitable for the imitation of genuine Manila paper which is prepared from the fibres of Manila hemp, *Musa textilis*. The first step in working jute in the form of cuttings or "butts," spinner's waste and bagging, is to cut up the material in a rag-cutting machine. The comminuted mass is then brought into a rag-boiler and for some time boiled under slight pressure—1½ atmospheres—with a comparatively large quantity of lime—25 to 35 per cent. of the weight of the jute. It is then washed in a half-stuff hollander and ground. As a rule, it is finally slightly bleached with chloride of lime.

UTILIZATION OF EXHAUSTED LYES AND THEIR NEUTRALIZATION.

The fluids which have served for the preparation of cellulose from wood contain, in addition to a considerable quantity of organic substance, the total quantity of mineral substances employed in their preparation. Partly for economic, and partly for hygienic, reasons, these substances have either to be reconverted into such products as can be again utilized in succeeding operations, or it must be endeavored to change them in such a manner that they may, without risk, be discharged into a natural watercourse, river or creek.

When working with the soda process, efforts are generally made to recover the soda as far as possible. The exhausted lyes contain the soda largely in the form of organic combinations which can be broken up by heat, carbonate of soda remaining finally behind, which may be again used for the preparation of lye. In order to recover the soda, the exhausted lyes are evaporated to dryness, and the resulting solid mass is calcined under the access of a strong current of air. The organic substance is thereby completely destroyed, the residue consisting of calcined (anhydrous) soda.

Since the evaporation of such large quantities of fluid as result in the manufacture of cellulose, requires a considerable amount of fuel, the apparatus used for the purpose should be so constructed as to allow of the heat produced being utilized to the fullest extent. Numerous propositions having more or less the object in view, namely, the saving of fuel, have from time to time been made. However, reverberatory furnaces are most frequently used for calcining the evaporated mass, the still very hot fire gases escaping from the furnace being utilized for heating shallow pans in which the lyes are constantly more and more concentrated, and finally converted into a solid mass ready for calcination in the furnace.

The quantity of soda recovered is of course considerably smaller than that originally used, a portion of it having been lost in the wash waters, but the latter do not contain enough of it to make their evaporation profitable. However, if the operation is properly conducted, from 60 to 66 per cent. of the soda used may be recovered. When working with the sulphite process, it is of the utmost importance to change the lyes so as to be able to discharge them, without risk, into running water. According to Mitscherlich, this is to be effected by greatly diluting the lyes, as well as the water used in washing the cellulose. However, it must be borne in mind that very large quantities of exhausted

lye are daily produced in a cellulose plant. Every quart of exhausted sulphite lye contains, in round numbers, 3 ounces of organic substance in solution and, in addition, the total quantity of mineral substances contained in the original lye.

However, since the lyes contain considerable quantities of sulphites which become decomposed in water, sulphuretted hydrogen being evolved, it will be readily understood that the waters of even a quite considerable stream will, in the course of time, become polluted to such an extent as to kill the fish inhabiting them, sulphuretted hydrogen being an exceedingly violent poison for them.

It would, therefore, seem absolutely necessary to neutralize the lyes as much as possible before discharging them into a water-course. According to a process proposed for this purpose by A. Frank, the exhausted lye from a boiling is mixed in a large cistern with a sufficient quantity of milk of lime to form neutral calcium sulphite which, being a salt that dissolves with difficulty, settles to the bottom, and after having been freed as far as possible from the fluid in a filter-press, can be re-used for the preparation of sulphite lye. The fluid having been separated from the neutral calcium sulphite is freed in another receptacle from the excess of lime by the introduction of smoke gases containing much carbonic acid, while the oxidation of a considerable quantity of organic substance is effected by conducting compressed air through the fluid. The fluid thus far purified is conducted upon an irrigation field and, after remaining there for some time, is discharged into running water. The calcium sulphite thus regained covers a considerable portion of the expense incurred in carrying out the process.

The sulphite lyes may also be utilized in tanning, but being of a very dark color, they impart this color to the leather, and besides make it brittle. However, this drawback may be overcome, and, according to a process proposed

by Hönig, the lye, previous to being concentrated by evaporation, is deprived of its color by treating it with zinc dust and sulphuric acid, a sufficient quantity of the latter to decompose all the sulphites contained in the fluid being required.

In carrying out this process, the resulting large quantities of sulphurous acid may, of course, be utilized for the preparation of fresh lye, a portion of the expense incurred being thereby covered.

IV.

VEGETABLE PARCHMENT.

When unsized paper, which should, however, contain no wood-pulp, is for a short time subjected to the action of quite concentrated sulphuric acid, the cellulose undergoes a peculiar physical change. The paper loses considerably in thickness, assumes a transparent appearance, becomes harder and acquires a condition reminding one of horn, becoming at the same time about five times as tenacious as the original material. When paper thus treated is moistened, it loses its rigidity and acquires the condition of animal bladder. If stretched tight and allowed to dry, it regains its former horn-like condition. The chemical composition of vegetable parchment is exactly the same as that of cellulose and, hence, the change effected by parchmentizing in the above-described manner is simply a physical one. Concentrated solution of zinc chloride produces the same parchmentizing effect as sulphuric acid, but in practice this process is not used, because it is far more expensive, and the complete removal of the poisonous zinc salt is far more troublesome than that of sulphuric acid.

The parchmentizing action of sulphuric acid is explained as follows: A solution of cellulose in concentrated sulphuric acid is first formed to a certain depth upon the surface of the paper, but so soon as the latter is taken from the sulphuric acid and brought in contact with a large quantity of water, the solution is immediately decomposed to free sulphuric acid and amyloid, the latter cementing the individual cellulose fibres together to a uniform mass. By this

cementation the paper acquires its extraordinary strength and transparent appearance.

NATURE OF THE PAPER TO BE PARCHMENTIZED.

For the production of vegetable parchment of the proper quality, paper especially made for this purpose has to be used, it being of the utmost importance that it should not contain a filling stuff of any kind, and that it consists of nothing else but cellulose. It must, therefore, neither be sized nor contain an addition of a foreign body.

In manufacturing paper intended for parchmentizing it has to be taken into consideration that its bulk is considerably decreased by the process, and hence it has to be made of sufficient thickness. To make the process of parchmentizing effectual, it is necessary for the paper to become completely impregnated with the acid the moment it comes in contact with it, it being only under these conditions that the momentary solution of the cellulose in the sulphuric acid takes place, not only upon the surface, but also throughout the entire bulk, of the paper. Hence paper to answer these requirements must, on the one hand, be of suitable thickness, and, on the other, should not be subjected to great pressure in passing through between the rolls. In this manner a loose, spongy paper is obtained, which is of comparatively little value for other purposes, but by reason of its porous, felt-like nature is especially well adapted for the preparation of vegetable parchment.

As previously mentioned, by bringing paper in contact with sulphuric acid an actual solution of cellulose in the acid takes place, which must, however, be again rapidly decomposed. This fact renders it impossible to impregnate the paper throughout its entire bulk when the latter exceeds a certain limit, because before the acid could penetrate into the interior, a comparatively thick layer on the surface would be completely dissolved. However, if parchment of greater thickness is to be prepared, recourse may be had to

a process which is based upon the fact that paper just parchmentized is very sticky when taken from the sulphuric acid bath. Two, three, or even four, breadths of paper are simultaneously subjected—each by itself—to the action of the sulphuric acid, and when taken from the latter are passed together—one on top of the other—between rolls, whereby, on the one hand, a considerable portion of adhering acid is squeezed out, and, on the other, the breadths of paper are inseparably cemented together.

SULPHURIC ACID USED FOR PARCHMENTIZING.

In order to obtain parchment of always the same quality, sulphuric acid of the same concentration and temperature has to be employed, and allowed to act upon the paper for a certain time. While the first-mentioned factors can be readily ascertained, the time during which the acid has to act depends largely on practical experience, and has to be fixed for every kind of paper by a few experiments on a small scale. Sulphuric acid of a specific gravity between 1.659 (58° Bé.) and 1.754 (63° Bé.) has, after many experiments, proved most suitable for use. Larger quantities of a fluid of the desired concentration are at one time prepared by mixing concentrated sulphuric acid with water, the mixture being allowed to stand by itself until its temperature is reduced to at least 60° F., because acid of a higher temperature acts too energetically upon the paper, and the latter might in consequence be readily converted into a slimy mass. Many manufacturers prefer even to work with acid of quite a low temperature because all the operations can then be carried on more leisurely.

The mixing of larger quantities of sulphuric acid with water being disagreeable work requiring great precaution, most of the manufacturers of parchment paper work with so-called chamber acid, which has a specific gravity in round numbers of 60° Bé., and can be directly used, besides being considerably cheaper than highly concentrated sulphuric acid.

When working with acid of 60° Bé., at a temperature not exceeding 60° F., five seconds' contact with the acid suffice for parchmentizing thinner varieties of paper. Thicker papers require a correspondingly longer time, and very thick papers are passed through the acid reservoir so slowly as to remain submerged upwards of 20 seconds.

It must, however, be borne in mind that by coming in contact with the paper, the acid in the parchmentizing vessel becomes slightly heated, and hence to prevent it from acting too energetically upon the paper, the velocity with which the latter is drawn through the acid has to be somewhat increased after the operation has for a short time been in progress.

When the paper has remained the required time in the acid it is as rapidly as possible withdrawn from the action of the latter, this being effected by bringing it in contact with large quantities of water, by which the acid is diluted to such an extent that the cellulose is no longer affected by it. The last remnants of sulphuric acid adhering to the parchment are removed by treatment with an alkaline fluid.

PARCHMENTIZING APPARATUS.

For the manufacture of parchment paper on a large scale, an apparatus is used, the essential features of which are as follows: The endless paper to be worked is wound on a roll from which it can be smoothly unrolled under a slight pull, and is next carried under glass rolls beneath the surface of the sulphuric acid, the latter being contained in a lead-lined trough. By arranging several rolls in the trough the paper is for a suitable time exposed to action of the acid, and is finally lifted from it in a perpendicular direction. As soon as it appears above the level of the fluid it is carried through between two rolls with sufficient pressure for the greater portion of acid to fall back into the lead-lined trough. The paper is now carried over glass rolls into a long trough filled with clean water, in which the greater

portion of still adhering acid is rinsed off. Since this first wash water becomes highly heated, it is advisable to charge the trough at the start with very cold water. From the first trough the paper reaches another one, in which it is further treated with water, it being best to have the water in this trough constantly running in a direction counter to that of the paper. This water absorbs but a very small quantity of sulphuric acid from the paper, and is allowed to run off from the wash-trough. It is advisable to sprinkle both sides of the paper, as it rises from the second trough, with fine jets of water from two horizontal pipes.

The last traces of acid still adhering to the paper are removed by passing it through a trough filled with water, which is constantly kept alkaline by small quantities of caustic soda lye or ammonia. After again being treated with clean water the paper is subjected to strong pressure between rubber rolls or wooden rolls covered with felt. It then passes between adjusting rolls, and finally reaches hollow iron rolls heated by steam for the purpose of drying the finished parchment.

While drying, the parchment has to be subjected to strong tension both lengthways and laterally, otherwise it would contract very much and acquire an uneven and wrinkled surface.

Since the sulphuric acid used in the preparation of parchment is only highly diluted, without being otherwise changed, provision should be made for its recovery. This can best be effected by having the first wash-trough into which the paper passes directly from the sulphuric acid vat, of but a small size and furnishing it with a large discharge valve, as well as with quite a large water-supply pipe. Two horizontal sprinkling pipes are also fixed over this trough.

When the content of acid in the first wash water has increased to such an extent as to amount to 20 per cent. of the entire quantity of fluid, the discharge valve and the

sprinkling pipes are opened. The contents of the trough run off in a few seconds, the acid being during this time washed from the paper by the sprinkling pipes. When the trough is empty, the discharge valve is immediately closed and the trough refilled with water by opening the cock of the large water pipe, the sprinkling pipes being finally closed. With a small-sized trough, a large valve, and a water pipe of considerable diameter, the discharge of the very acid water, as well as the refilling of the trough is so rapidly effected that the supply of water furnished during this time by the action of the sprinkling pipes is sufficient and the operation need not be stopped, and thus very large rolls of endless paper can, without interruption, be made into parchment.

The wash water from the first trough when it contains about 20 per cent. of sulphuric acid, can be readily worked to sulphuric acid of 60° Bé., it being only necessary to evaporate it in a shallow lead pan heated by steam till the acid has acquired its ordinary concentration. When working with the more concentrated commercial sulphuric acid, the wash water is utilized in place of pure water, for diluting the acid. However, as in this case, an excess of sulphuric acid would before long accumulate in the factory, it is advisable to use, instead of ordinary commercial acid, fuming sulphuric acid, the latter by reason of its content of sulphur trioxide requiring much more water for dilution to 60° Bé.

PROPERTIES OF PARCHMENT PAPER.

By the conversion of ordinary paper into parchment its bulk is considerably decreased as well as its content of ash, but its specific gravity is much increased. The principal feature, however, is the increase in absolute strength, which makes parchment especially suitable for book bindings and all other purposes for which strength is a requisite. The changes paper undergoes by parchmentizing are shown for three different varieties of it, in the table below:

	Thickness millimeters.	Specific gravity.	Absolute strength per square millimeter Kilogrammes.	Content of moisture per cent.	Content of ash.
Raw paper . . .	0.234	0.617	1.415	6.785	0 633
Parchment paper.	0.152	0.964	6.436	8.778	0.496
Raw paper . .	0.178	0.543	1.483	7 071	0.645
Parchment paper.	0.113	0.937	5.111	8.483	0.458
Raw paper . . .	0.134	0.624	1.503	6.978	0.678
Parchment paper.	0.088	0.927	5.777	9.160	0.559

As previously mentioned, the preparation of parchment of special thickness presents some obstacles, it being difficult to saturate in a short time thick paper with sulphuric acid and to remove the latter rapidly. In this case two or more breadths of paper are treated, each by itself, with sulphuric acid and the first wash water, and then passed together, under quite heavy pressure, between rolls. The surfaces of the breadths of paper are at this time still sufficiently sticky to make it possible to combine the breadths so intimately to a single one, that the joint cannot be seen even by examining the cross section of the dried parchment with the microscope. By the use of an apparatus of suitable construction, as many as four breadths may thus be combined in one and, though the thickness of the latter does not exceed that of ordinary drawing paper, its strength is actually surprising. Particular care must be taken in washing parchment of such special thickness, as it would in a short time be decomposed if a small quantity of sulphuric acid should happen to remain in its interior.

RENDERING PARCHMENT PAPER FLEXIBLE.

If parchment paper is to be deprived of its characteristic stiffness and hardness and to be rendered flexible, the object may be attained by suitable treatment with strongly hy-

groscopic bodies, glycerin being especially adapted for the purpose, as it is perfectly harmless and there can be no objection to the use of a material treated with it, for wrapping up articles of food. Parchment not intended for the latter purpose may be rendered flexible by the use of a concentrated solution of magnesium chloride, calcium chloride or of another highly hygroscopic salt. The operation is carried on as follows: The finished parchment, before it has been dried, is allowed to run over a roll dipping partially into a vessel containing concentrated glycerin, a thin layer of the latter, regulated by a scraper, adhering to the roll and being transferred to the parchment. Parchment thus treated does not contract very much in drying and remains flexible to a certain degree.

By reason of its great density parchment paper is easily colored, the separation of the coloring matter in it being readily effected by placing it in a suitable solution. Aniline colors are generally employed, fuchsin being used for red. The alcoholic solution of fuchsin is poured into boiling water and when thoroughly distributed in it, the parchment is introduced. For blue, water-soluble blue or indigo carmine is used; for violet, aniline-violet, or the parchment is first colored red and then blue. Yellow is obtained with picric acid; orange, with fuchsin and picric acid; and green, with picric acid and indigo-carmine.

The behavior of vegetable parchment towards the ordinary adhesive agents, such as mucilage, paste, glue, etc., is very unfavorable, they either do not adhere at all or crack off very readily. A somewhat better adhesion is effected by first applying alcohol, and then the adhesive agent to the parts of the parchment to be joined together, or by laying a strip of very thin ordinary paper between them. The best material for the purpose of joining together parchment paper is chromium glue, prepared by allowing glue to swell up in water to which a quantity of potassium dichromate equal to 2 per cent. of the weight of the dry glue has been

added. When swelled up, the glue is dissolved by heating in water, the solution being kept in the dark until used. Chromium glue is used by coating the pieces to be joined with the solution, pressing them together and exposing them to the light, the chromium glue being thereby converted into an insoluble combination which only swells up, without, however, dissolving if brought, even for a longer time, in contact with water.

Vegetable parchment finds many applications. It is made into very strong pads for certain important writings, is employed for the manufacture of receptacles for articles of food, for instance, sausage casings, further for durable book bindings, etc., and large quantities of it are also used for osmotic purposes, it possessing the property of allowing the passage of fluids, such as solutions of salt, sugar, etc.

VULCANIZED CELLULOSE (VULCANIZED FIBRE).

Under this name a material is brought into the market by some English factories which, as regards its properties, is claimed to be very suitable as a non-conductor of heat and for insulating electric lines. According to Foster it consists essentially of a product which, as regards its mode of manufacture, closely resembles vegetable parchment, but it has the advantage that it can be made in pieces of any desired thickness, which with vegetable parchment can only be done within very narrow limits.

According to the description, vulcanized fibre is prepared by treating cellulose in a loose form, or in the form of paper, with a fluid consisting chiefly of sulphuric acid, to which, however, have been made such additions as will neutralize the progressive action of the acid when allowed to remain for a longer time in contact with the vegetable fibre. This is claimed to be attained by dissolving metallic zinc, and next dextrin, in the sulphuric acid. According to the patent specification, the process is as follows: For every 32 parts of ordinary sulphuric acid 1 part zinc is used, the mixture

being allowed to stand quietly till all the zinc is dissolved and the fluid has again acquired the ordinary temperature. In the fluid thus obtained, which represents a solution of zinc sulphate in an excess of sulphuric acid, dextrin is dissolved, the proportion used being 1 part of dextrin to 4 parts of solution.

While, as previously mentioned, the adhesive power of paper treated with sulphuric acid alone, disappears in a short time so that haste has to be made in combining two or more breadths of paper, paper treated in the above-mentioned solution retains its adhesive and cementing powers for a much longer time, so that any number of breadths can be leisurely combined to one plate, or loose cellulose may be shaped. The finished articles are first treated with solution of common salt in water, and finally completely freed from adhering salts by long-continued washing with water. In the common-salt bath a transformation is claimed to take place, so that sodium sulphate and zinc chloride are formed which can be readily removed by washing.

Very thick plates or other thick articles may, it is claimed, be prepared from the mass by coating the parts to be cemented together with the above-described solution, by which they are rendered adhesive and can be made into a single piece by pressing or rolling.

Vulcanized fibre is found in commerce in two forms, namely, as a hard mass closely resembling wood in its properties, and as a soft, flexible and elastic substance behaving similarly to leather. The hard mass can be worked with the knife and saw, can be planed and turned, and, in a fresh state, can by pressure be molded into any desired shape; two pieces may be glued together like wood. On account of being insensible to moisture and air, and by reason of its exceedingly slight power of conducting electricity, the mass is claimed to be especially suitable for the manufacture of insulators for electrical purposes. The elastic mass is recommended for all purposes for which, at

the present time, leather or vulcanized rubber is generally used, for instance, for packing, valves, etc.

In the description given above the statements made in the patent specifications have been accurately followed, and an attempt has been made to prepare vulcanized fibre in accordance with them, but entirely satisfactory results could not be obtained. While it cannot be denied that parchmentizing in the fluid containing zinc and dextrin takes place more slowly than when working with sulphuric acid alone, it was impossible to obtain a mass approaching in solidity that of wood, or even of horn. The incompact masses could be quite completely freed from the acid and salts by repeated treatment with water, but this was very incompletely the case with the masses subjected to stronger pressure, so that in drying they fell to pieces by reason of sulphuric acid remaining behind. These observations justify the conclusion that several things essential for the preparation of the vulcanized fibre mass have not been given in the patent specification, and that the product cannot be made by simply following the statements contained therein.

V.

PRODUCTION OF SUGAR AND ALCOHOL FROM WOOD-CELLULOSE.

The fact that cellulose may be converted into fermentable sugar by boiling it for some time with dilute mineral acid has been known for a long time. Although, theoretically, the conversion of cellulose into sugar appears a very simple process, in practice on a large scale numerous difficulties are encountered. Although the first experiments in this direction were made as early as 1854, no process has been discovered up to the present time which could be used on a large scale with any prospect of success. Nevertheless, it would not seem that a mistake is made in saying that with the preparation of fermentable sugar from cellulose it will be exactly the same as with the production of pure cellulose from wood, several processes for that purpose being now known after many unsuccessful experiments had been made, and that a method for the production of fermentable sugar from wood-cellulose, which can be practically applied, will also be finally found.

'In all the attempts to obtain fermentable sugar from cellulose, wood has heretofore been employed as the initial material, and that the results obtained with its use have comparatively given but little satisfaction, may possibly be chiefly due to the fact, that in the wood the individual vascular bundles, consisting of cellulose, are so firmly cemented together by the lignin as to make them in a high degree proof against the action of chemicals.

Since a way for the destruction of the lignin and rendering the cellulose accessible to the action of chemicals has

been found in the progress made in this direction in the manufacture of cellulose, it seems reasonable to suppose that the time is drawing nearer when the question as regards the production of larger quantities of fermentable sugar from cellulose, relatively wood substance, will also be solved.

OLDER METHODS.

The first attempts to produce on a larger scale fermentable sugar from wood were made by Zetterlund. He used fir sawdust and boiled it with 8 per cent. of its weight of hydrochloric acid under a pressure of $1\frac{1}{2}$ pounds per square inch. After boiling for 8 hours, a fluid containing 3.38 per cent. of dextrose was obtained, and after 11 hours, 4.38 per cent. Calculated to sawdust, 19.67 per cent. of the latter had been transformed. The fluid, after being separated from the solid residue, was neutralized with soda and then contained a quantity of common salt equal to the quantity of hydrochloric acid used. The fluid was brought into fermentation with yeast prepared from 22 pounds of malt extract and the fermented mass was subjected to distillation. The yield of alcohol from 990 pounds of sawdust amounted to 26.5 quarts.

As will be seen from the figures given above, there is a considerable increase in the quantity of sugar obtained when boiling is continued for more than 8 hours. As the correct basis for an explanation of this increase, it may well be assumed that at the beginning of the action of the hydrochloric acid upon the wood, the tendency of the entire chemical process was to attack the lignin by the acid and hence, as a preparatory operation, a gradual laying bare of the vascular bundles took place. Only after this process had progressed to a certain extent, the acid commenced to act upon the cellulose itself, a much more abundant formation of sugar taking place than in the former period.

There can scarcely be any doubt that with the use of a higher pressure and longer boiling, far larger quantities of

sugar can be obtained from the wood than with Zetterlund's process.

Since, for the purpose of obtaining cellulose, the disintegration of the wood may also be effected by acid, Bachet and Machard attempted to combine the production of sugar and cellulose in one process, so that the sugar solution might, in a certain measure, be obtained as a by-product in the manufacture of cellulose. (See p. 51).

According to their process, the wood is boiled with dilute acid, the acid together with the sugar formed washed out with water and the remaining mass is comminuted in a hollander, bleached with chlorine gas and finally treated with soda lye. The product thus obtained cannot be called either mechanical pulp or cellulose, it being an intermediary between both products but, as regards its properties, approaches more closely bleached mechanical pulp than cellulose. On a large scale the operation is carried on as follows: The wood—fir or pine—is cut into thin discs. Four thousand four hundred pounds of these discs are brought into a vat together with 2,000 gallons of water and 1,760 pounds of crude hydrochloric acid, and boiled for 12 hours by direct steam, hence under ordinary pressure. The resulting fluid having been separated from the solid contents of the vat, is neutralized with upwards to 99 per cent. of calcium carbonate and fermented in the usual manner. By distilling the fermented fluid, a corresponding quantity of alcohol is produced, it being, however, not stated how large a quantity of it is obtained from the 4,400 pounds of wood used.

It is remarkable that according to Bachet and Machard's statements, neutralization of the acid should be effected by lime, since the fluid must then contain a corresponding quantity of calcium chloride, and it is very questionable whether the fermentation of the sugar can proceed regularly in the presence of such a large quantity of a calcium salt.

In addition to the processes above described, there are some other methods for the production of alcohol from wood, of which, however, but little is known, very likely for the reason that satisfactory results were not obtained. One of these methods relates to the production of alcohol from beech. In this case, dilute sulphuric acid is made use of for the formation of sugar. Boiling is effected under a comparatively high pressure—7 to 8 atmospheres—and continued for 10 to 12 hours. The final result was a comparatively very small yield of raw alcohol of a disagreeable odor, while the solid mass which remained in the boiler showed a dark-brown color, had a disagreeable odor, and was not fit for anything but fuel.

The failure of this experiment may be explained from the process itself. At the high temperature which a fluid standing under a pressure of 7 to 8 atmospheres must acquire before it reaches the boiling point, the sugar already formed is again changed, and the production of a larger quantity of it entirely excluded. The poor quality of the raw alcohol obtained may be due to the properties of the wood used, beech containing a very large quantity of extractive substances, which by the action of sulphuric acid very likely yield bodies of a disagreeable odor characteristic of the raw alcohol. That amongst these bodies are such as gradually acquire a dark color under the influence of the air, is shown by the fact that the raw alcohol in a very short time became dark brown. By repeated rectification, this disagreeable odor could only be diminished, its entire removal being impossible, and neither could the alcohol by rectification be brought to a state in which it remained colorless, becoming wine-yellow when for a short time exposed to the air.

NATURE OF THE WOOD TO BE WORKED.

The nature of the wood to be worked appears to exert great influence upon the yield of alcohol in general, as well

as upon the quality of the product itself. Experiments made in this direction with pure cellulose gave much more satisfactory results than with wood itself, and the alcohol obtained could be quite readily purified by rectification. These facts serve as hints of how to proceed in order to obtain comparatively large yields of alcohol of sufficient purity, as well as that great care has to be exercised in the selection of the wood to be used.

Compact, heavy wood, containing large quantities of extractive substances may at the outset be designated as unsuitable for the purpose. Such wood contains considerable quantities of lignin, tannin, coloring matter and other extractive substances which cannot be converted into sugar, and hence beech, oak, chestnut, etc., are not available.

The conifers—pine, fir, spruce, etc.,—contain large quantities of rosin and volatile oils, the presence of which has a disturbing effect. Hence there is but little choice as regards the selection of wood for the production of alcohol, and only varieties with a white, incompact and soft wood can be used to advantage. Of the European varieties of wood, aspen, poplar, willow and linden, are the most suitable materials for the purpose.

A few remarks may here be made in reference to the apparatus to be used and the mode of procedure in general. Since in starting a plant as, for instance, one required for working wood, machinery plays an important part, the entire execution of the plan is generally left to an engineer who puts up apparatus, boilers for boiling under pressure, etc., according to his own judgment without consulting the chemist as to the conditions the apparatus is to meet. The order in which the plant is to be managed is also, as a rule, indicated by the engineer who, in most cases, does not possess the chemical knowledge, which is absolutely required if favorable results are to be obtained.

Thus it may happen, as it actually did in the above-mentioned example, that wood is boiled under pressure

with a comparatively very large quantity of sulphuric acid, the temperature becoming thereby so high that the newly-formed sugar was largely reconverted into other combinations and the yield in consequence was so small, that the entire expensive plant had to be abandoned and the machinery sold for old metal.

MORE MODERN METHODS.

If the working of wood for the production of alcohol is to be carried on in a rational manner, *i. e.*, in accordance with the laws of chemical science, it is absolutely necessary to proceed according to the following principles:

The soft, white wood cut into thin discs should for a considerable time be submerged in running water, the object of this soaking being to free the wood as much as possible from water-soluble extractive matter such as albumen, tannin and other substances, so that only the vascular bundles cemented together by the lignin remain behind.

The wood when sufficiently soaked is to be cut into small pieces as if it were to be worked for cellulose by the soda or sulphite process. This reduction is necessary, on the one hand, to give the wood a very large surface, thus presenting to the acid many points of attack, and on the other, because the residue which remains behind after treating the wood with acid, can thus be best utilized for the preparation of cellulose.

Hydrochloric acid is most suitable for converting the cellulose into sugar, it being preferable to sulphuric acid, if only for the reason that even at a high temperature it does not form brown, coal-like combinations from the cellulose.

Since by boiling under increased pressure a much larger quantity of sugar can be obtained than by boiling under ordinary conditions, an increased pressure will have to be worked with, and the use of a closed boiler would, therefore, seem to be one of the conditions for attaining favorable results.

For boiling, a vertical, iron vessel furnished with a removable lid, steam heating and safety-valve will have to be used. Since iron is vigorously attacked by the vapors of hydrochloric acid, the boiler will have to be lead-lined, this metal being least attacked by the vapors. In order to save the lead-lining, a wooden vessel which almost fills the boiler, may be placed in the latter. This wooden vessel serves for the reception of the comminuted wood and the fluid, and when boiling is finished and its fluid contents have been discharged, it is lifted from the boiler by means of a hoist.

When the boiler has been charged with the comminuted wood and dilute hydrochloric acid, the apparatus is closed air-tight and the fluid is brought to boiling by means of steam of such a tension that the contents of the boiler are not heated to above 230° or 233.6° F., boiling being continued for a suitable time, and very likely 10 to 12 hours will be required until a sufficiently large quantity of sugar will have formed. There being no data on hand regarding the time required for obtaining the largest possible quantity of sugar, and this time varying probably for every variety of wood and for different concentrations of the acid, it must be determined by experiments. Such experiments or tests are made by taking every hour samples from the boiler and determining the content of sugar. If, in the disintegration of wood, the conditions should be similar to those in the disintegration of starch for the purpose of producing grape-sugar, it will be observed by the samples that the quantity of sugar formed within a certain time increases quite regularly until a period is reached when the further formation of sugar becomes very sluggish, so that for reasons of expediency the operation may be considered finished.

Since the hydrochloric acid does not undergo a change in converting a portion of the cellulose into sugar, but acts by its mere presence, the fluid at the end of the operation will

contain as much free hydrochloric acid as was originally present, and this acid has to be removed as far as possible. This may be effected, when the formation of sugar is complete, by connecting the lid of the boiler with a lead cooling coil in a cooling vat, and distilling off a portion of the fluid, boiling being continued under the ordinary pressure. The greater portion of the hydrochloric acid present in the fluid will thereby escape together with the steam, and will be again condensed in the cooling coil. The dilute hydrochloric acid thus obtained may be used for the next operation. Distillation may be continued until the fluid contains only 3 per cent. of free acid, when the operation is interrupted.

When this point has been reached, the fluid is discharged from the boiler, the boiling vessel hoisted from the latter, and replaced by another which has in the meantime been charged with wood, so that with the exception of the short time required for emptying and recharging the boiler, the operation can be carried on without interruption.

The unchanged wood remaining in the boiler is still saturated with the acid, saccharíferous fluid. This fluid is obtained by repeatedly washing the wood with water, but it cannot be recommended to combine it with the fluid first obtained, otherwise the sugar solution would be too much diluted. The fluid used for washing the wood is utilized in the next operation in place of pure water, the hydrochloric acid as well as the sugar contained in it being thus completely exhausted.

The sugar solution discharged from the boiler is now neutralized with soda to such an extent that its content of free hydrochloric acid is reduced to 1 per cent., the composition of the fluid being then such that yeast can live in it, provided it is furnished with the requisite quantity of nourishing salts.

This object may be attained by adding to the fluid cooled to about 86° F., 5 per cent. of yeast prepared from crushed

malt. It is, however, also possible to make use of a cheaper method by adding directly to the fluid salts serving as nutriment of the yeast, equal parts of potassium phosphate and ammonium phosphate being very suitable for the purpose. One part of the nourishing salt for 1000 parts by weight of the fluid is used. These salts dissolving with ease in water, a solution of them is prepared in a small quantity of the fluid and uniformly distributed throughout the sugar solution by stirring.

Fermentation can be induced either by freshly-compressed yeast or by freshly-prepared distillery yeast. With the fluid at a temperature of 86° F., propagation of the yeast takes place very rapidly, and in a short time the fluid is in a state of vigorous fermentation. Regarding the quantity of compressed yeast to be used it may be said that ¼ part by weight of it suffices for 100 parts by weight of the sugar contained in the fluid.

The fluid is now left to itself until fermentation is finished, which with the high temperature at which it was induced, will be the case in, at the utmost, 36 hours. It is then drawn off from the yeast at the bottom of the vat, and immediately subjected to distillation. The yeast need not be removed from the vat but can be utilized in the next operation.

Distillation of the fermented fluid should be effected in an apparatus which allows of the alcohol being rectified as far as possible, *i. e.*, to somewhat above 96 per cent. Wood alcohol always has a peculiar odor due to small quantities of combinations, the chemical nature of which is not definitely known. However, by careful rectification these bodies can be so completely separated from the alcohol that it possesses only the odor of the pure product.

When soft, white varieties of wood are in the above described manner treated with hydrochloric acid, the residue remaining behind retains its color unchanged, provided the acid used is free from iron. However, ordinary crude

hydrochloric acid, which will have to be used when working on a large scale, always contains a certain quantity of iron, and the wood shows generally a slightly brownish color, so that when further worked to cellulose it does not yield an entirely pure white product, which can, however, be so made by bleaching.

Supposing that 20 per cent. of the weight of the wood can be converted into fermentable sugar, and assuming that this quantity of sugar after fermentation and deduction of unavoidable losses yields in round numbers 10 liters of alcohol: by taking the value of 1 liter of alcohol at only 10 Pfennige * it will be seen that the alcohol obtained from 100 kilogrammes (220 lbs.) has a value of 1 mark,† and that the remaining 80 kilogrammes (193.6 lbs.) of wood are available for further working into cellulose. Hence the calculated results, even with such small yields and low price of the alcohol produced as have been assumed above, are by no means unfavorable, and it might certainly prove a profitable undertaking for a chemist to investigate closely the subject, working especially with a view towards increasing the yield of sugar from the wood.

CLASSEN'S PROCESS.

The chemist Classen has recently devoted much time to the solution of the problem of producing directly-fermentable sugar from wood, having adopted entirely new methods, which, according to his statements, have actually resulted in comparatively large yields.

According to a process patented by him the wood is first treated with sulphuric acid, having a concentration of the so-called chamber acid—50° to 60° Bé.—and then submitted to powerful mechanical pressure, the effect of the latter, it is claimed, being to convert a large portion of the

* 1 Pfennig = 0.236 cent.

† 1 Mark = 23.6 cents.

cellulose contained in the wood into dextrose. (?) The mass need then only be diluted with water and boiled for some time at the ordinary pressure to accomplish complete (?) conversion into dextrose.

Air-dry sawdust, which in this state contains in round numbers 15 per cent. of water, is used as raw material. A portion of the sawdust is intimately mixed with three-fourths its quantity of sulphuric acid of 57° Bé., a mass of a peculiar greenish color being thereby formed. By extracting this mass with water a fluid is obtained in which no sugar can be found. By subjecting it, however, to strong pressure by means of a powerful hydraulic press a vigorous chemical reaction takes place, the mass becoming highly heated and its color being changed to nearly black, so that it presents the appearance of wood which has been carbonized by highly concentrated sulphuric acid. On extracting the pressed mass with water the latter shows a very distinctive sugar-reaction.

According to close investigations, it is claimed that in consequence of the pressure, the greater portion (?) of the wood-fibre is converted into cellulose, and in addition there are present other bodies which, as regards their properties, occupy intermediate positions between dextrin and dextrose. For the conversion of all (?) the dissolved bodies into dextrin, it suffices to mix the pressed mass with water in the proportion of 1 part of the substance originally used to 4 parts of water, and to boil it for half an hour in an open vessel. By this process a fluid is said to be obtained which is free from the intermediate products interfering with fermentation otherwise found in dextrose solutions prepared from wood.

If the process above described is actually available in practice, it may be supposed that the first effect produced by the sulphuric acid upon the wood is to destroy the encrusting substance—the lignin—so that the pure cellulose becomes accessible to the further action of the acid. It re-

mains still to be established by experiments, whether the conversion of this cellulose into dextrose cannot be attained by simply heating the green mass to a certain temperature without the use of strong pressure.

A decided disadvantage of this process is, however, the use of a quantity of sulphuric acid which is exceedingly large in comparison with the quantity of wood to be worked, amounting in round numbers to 75 per cent. of the latter; and to bring the dextrose solution finally obtained into fermentation, this quantity of sulphuric acid must be nearly neutralized by the addition of lime. Hence, it will be necessary to recover the considerable quantity of dextrose solution adhering to the resulting gypsum by systematic washing of the latter. The quantities of gypsum which would finally accumulate in carrying on the operation on a more extensive scale, would be very large and difficult to utilize, so that the cost of producing fermentable sugar according to this process would be comparatively quite high.

It would appear that the inventor of the above-described process was himself not entirely satisfied with the results, and continued his investigations in regard to the production of dextrose from wood in another direction. A noteworthy process, also patented by Classen, is based upon the principle that by the action of watery sulphurous acid at a higher temperature, wood-substance is disintegrated to such an extent that the presence of a very small quantity of sulphuric acid suffices for the conversion of a very considerable quantity of cellulose into fermentable sugar.

In the commencement of the operation a fluid consisting of a concentrated solution of sulphurous acid containing 0.2 per cent. of sulphuric acid is used, or sulphurous acid alone is employed, the latter, at a certain stage of the process, being partially converted into sulphuric acid so that at the moment of its nascency it acts upon the cellulose.

The maximum yield of dextrose is obtained by conduct-

ing the operation so that the formation of sulphuric acid takes place at a period when the temperature in the boiler is between 248° and 293° F. In this case, it is claimed, that from every kilogramme (2.2 lbs.) of wood (dry substance) at least 300 grammes (10.58 ozs.) of dextrose are obtained, of which, on an average, 80 per cent. is fermentable. Hence, in round numbers 120 grammes (4.23 ozs.) of absolute alcohol would be obtained from 1 kilogramme (2.2 lbs.) of anhydrous wood-substance.

The temperature required for the formation of dextrose after the wood has been previously disintegrated by the action of sulphurous acid, depends on the nature of the wood to be worked, a temperature of 267° F. sufficing for birch, while for fir one of upwards to 293° F. is necessary. While a certain quantity of dextrose is without doubt formed below these temperatures, it is a comparatively very small one.

The production of sulphuric acid at a certain stage of the process may be effected in various ways, the simplest method being to introduce into the vessel atmospheric air or a gas mixture rich in oxygen, or by adding manganese suboxide or peroxide, which yield a portion of their oxygen, a corresponding quantity of sulphurous acid being thereby converted into sulphuric acid.

From what has been said above, the main point of the process consists in treating the wood in an autoclave with the sulphurous acid solution until the temperature reaches 248° to 293° F., then bringing about the formation of sulphuric acid and continuing heating for 10 to 15 minutes longer.

Although Classen appears to lay great stress upon the fact that the sulphuric acid acts at the moment of its formation upon the cellulose, he remarks directly in connection with the description of his process given above, that in place of sulphuric acid, a mixture of sulphurous acid with some other inorganic acid, for instance, hydrochloric acid of a

concentration of 0.2 per cent. or more, may also be used. If such is actually the case, the particular action which the sulphuric acid is claimed to exert at the moment of its formation, is virtually eliminated, and the use of sulphurous acid for the disintegration of the wood remains as the only main feature of the entire process. It must be admitted that the figures given above regarding the yield of fermentable sugar are excellent, and for this reason alone the process deserves serious consideration.

Experiments made by Classen to effect the disintegration of the wood by means of chlorine or hypochlorides yielded favorable results also. The wood, together with a half per cent. chlorine water, is heated to between 248° to 293° F., and sulphurous acid is then introduced into the vessel and rapidly converted into sulphuric acid by the action of the chlorine.

Another process, also patented by Classen, consists in the action of sulphuric acid, just formed from sulphuric anhydride, upon the wood. Vapors of sulphuric anhydride mixed with vapors of sulphur dioxide are conducted upon the moist sawdust. The sulphur dioxide on coming in contact with the water contained in the sawdust is converted into sulphurous acid, and the wood is by the latter disintegrated in the manner already explained. The sulphuric anhydride on coming in contact with the water is transformed to sulphuric acid, which at the moment of its formation is said to possess great inverting power. Classen claims to effect the treatment of the wood with sulphuric anhydride in revolving lead-lined drums, and accelerates the operation by previously heating the drums to from 86° to 104° F. The resulting mass is then pressed until it is hard and of a dark color, when it is treated with four times its quantity of water, and after neutralization of the acid is subjected to fermentation. Classen has found it suitable to heat the mass treated with sulphuric anhydride for some time in a closed vessel to between 257° and 275° F., the formation of sugar being thereby still further increased.

Sulphurous acid possessing in an uncommon degree the property of checking fermentation, it would appear absolutely necessary to free the fluid containing dextrose completely from it before submitting it to fermentation, and this can only be with certainty effected by boiling continued for a longer time. Only when a test of the fluid as to the presence of sulphurous acid yields a negative result, the free acid still present can be almost completely neutralized, and the fluid set for fermentation. The presence of a smaller quantity of acid does not impede fermentation, but is rather beneficial, since yeast thrives very well in an acid fluid, while certain other organisms, which bring about by-fermentations, cannot develop it.

A further modification of Classen's process consists in the wood being simultaneously exposed to the action of two acids at the moment of their liberation. The wood is first heated, together with sulphurous acid, to between 266° and 293° F., then allowed to cool to 248° or 266° F., when chlorine water is introduced into the fluid. In this case, sulphuric acid, as well as hydrochloric acid, is formed, and the presence of both of these acids is said to have a favorable effect upon the conversion of cellulose into dextrin. The quantity of chlorine to be used must be sufficiently large, so that at least 0.2 per cent. of sulphuric acid is formed.

If, as previously stated, 120 grammes (4.23 ozs.) of pure alcohol can be obtained from 1 kilogramme (2.2 lbs.) of perfectly dry wood-substance by one of Classen's processes, it would be well adapted for working on a large scale. Regarding the residue of substance not converted into dextrose, it could very likely not be utilized for any other purpose than for burning under the boilers of the plant.

VI.

PREPARATION OF OXALIC ACID FROM WOOD CELLULOSE.

When an organic substance is heated, together with caustic alkalies, to a certain quite high temperature, it is completely decomposed, and among the products of decomposition is always found a certain quantity of oxalic acid. The organic substances behave thereby, however, in such a manner that from bodies of animal origin but small quantities of oxalic acid can be obtained, while substances derived from the vegetable kingdom yield such a large quantity of it that it may almost be designated as the chief product of the processes of decomposition. A series of exact experiments with various substances of vegetable origin have led to the result, that the yield of oxalic acid is the greater the more closely the vegetable substances used approach the pure carbohydrates in their composition.

In accordance with this, starch, pure cellulose, etc., give comparatively the largest yields of oxalic acid. Since, in addition to cellulose and lignin, wood contains but small quantities of other bodies, it is especially suitable for the preparation of oxalic acid, and the more so as sawdust, which otherwise is of but little value, is the best material for the purpose. Though there is considerable difference in the various kinds of wood as regards the extractive substances contained in them, oak being, for instance, very rich, and poplar very poor in them, this fact exerts but little influence upon the yield of oxalic acid, which justifies the conclusion that the extractive substances—tannin, coloring matter, etc.—as well as the wood-substance itself, may

be converted into oxalic acid. Since all substances containing cellulose form an equally good material for the production of oxalic acid, all waste products of this kind may be used, and in addition to sawdust, waste from the manufacture of wood-cellulose and vegetable parchment, as well as scraps of tissue of vegetable origin may be utilized.

The formation of oxalic acid from the above-mentioned substances takes place by heating them together with a certain quantity of caustic alkali—potassium or sodium hydroxide, or a mixture of both—to above 392° F. It may, however, be mentioned as a remarkable fact that sodium hydroxide, when used by itself, gives but a very small yield of oxalic acid, while caustic potash forms considerably larger quantities, and the best results are obtained when both the alkalies, mixed in a certain proportion, are allowed to act upon the saw-dust. There is no theoretical explanation of these facts, which have been established by experiments made with the greatest exactness.

THORN'S INVESTIGATIONS.

According to investigations made in this direction by Thorn, 50 parts of sawdust heated with 100 parts of caustic soda to a temperature of 392° F. yield a quantity of crystallized oxalic acid equal to 36 per cent. By doubling the quantity of caustic soda a greater yield is obtained. Thus 25 parts of sawdust heated with 100 parts of caustic soda yielded, when melted in a dish at a temperature of 464° F., a quantity of oxalic acid which, calculated to 100 parts of sawdust, amounted to 42.30 per cent. However, an experiment made with the same quantities of both substances spread out in a thin layer and heated to 464° F. resulted in a yield of 52.14 per cent.

Further investigations by Thorn refer to the quantities of oxalic acid which can be obtained by the action of a mixture of caustic soda and caustic potash upon sawdust. Thorn extended these investigations still further by examin-

ing into the behavior of the various mixtures when they were melted together with sawdust in dishes, or when the masses were heated in thin layers. The figures indicating the yield of oxalic acid under these different conditions give at the same time a hint of how the manufacture has to be carried on in order to obtain the greatest possible yield.

1. Yields of oxalic acid by heating sawdust with a mixture of caustic soda and caustic potash in thin layers—2 parts of alkali hydroxide to 1 part of sawdust were used.

Proportion between caustic potash and caustic soda.		Temperature, ° F.	Yield of oxalic acid from 100 parts of wood.
20	80	374	19.78
20	80	392	21.50
20	80	464	30.04
30	70	374	21.38
30	70	464	38.39
40	60	374	14.00
40	60	392	30.35
40	60	464 to 473	43.70
50	50	392	25.76
50	50	464 to 473	39.04
60	50	392	30.57
60	40	464 to 473	42.67
80	20	392 to 428	45.59
80	20	464	61.32
90	10	464	64.24
100	—	464 to 473	65.57

By treating the sawdust with one of the mixtures of caustic alkalies given above, its color is changed as soon as the temperature exceeds 284° to 302° F., becoming at first brownish, which soon yields to a greenish-yellow tone. The mass then acquires a pasty condition, and at 356° F. evolves heavy nebulous vapors. That at this temperature reaction commences to be most energetic is evident from the fact that the action continues even if further heating is entirely interrupted. The temperature of the mass then gradually rises to above 680° F., the mass swells up, evolves a large quantity of combustible gases and finally

carbonizes completely when a mixture of 90 parts of caustic soda, 10 parts of caustic potash and 50 parts of wood has originally been used. This proves that with the use of a mixture containing such a small quantity of caustic potash the production of somewhat larger quantities of oxalic acid would be impossible as the temperature of the mass could not be regulated.

In the same degree as the quantity of caustic potash in the mixture is increased and that of caustic soda is decreased, the reaction takes place less violently, and it is possible to maintain the temperature of the mass within the limit of 464° F.

According to the series of figures given above the best proportion between caustic potash and caustic soda would be to use 80 parts of caustic potash to 20 parts of caustic soda, or 90 parts of the former to 10 of the latter. The temperature has to be raised to above 464° F. in order to obtain a yield of over 60 per cent. of oxalic acid.

As will be seen from the above-mentioned figures, a considerably larger yield of oxalic acid is obtained, if the mixture be heated in a thin layer, the great advantage of this mode of procedure, when working on a large scale, consisting in the fact that the temperature of a mass can be more readily kept within the prescribed limits than when working in deep vessels. For this purpose, Thorn has determined the following proportions:

Proportion between caustic potash and caustic soda.		Temperature. ° F.	Yield of oxalic acid from 100 parts of wood.
0	100	392 to 408	33.14
10	90	446	58.36
20	80	464 to 494	74.76
30	70	464 to 494	76.77
40	60	464 to 494	80.57
60	40	464 to 494	80.08
80	20	473	81.24
100	0	464 to 494	81.23

Solutions of quite high concentration (40° Bé.) of the

caustic alkalies containing potash and soda in appropriate proportions are first prepared, and heated to the boiling point. The sawdust is then introduced, the proportions being so chosen that for 2 parts of alkali hydroxide one part of wood is used. In introducing the sawdust care should be taken to see that it is uniformly distributed throughout the fluid and, if the latter had a concentration of 40° Bé., it will be completely absorbed by the sawdust.

The mixture is then evenly spread out upon iron pans in layers not exceeding 0.39 inch in thickness and heated as uniformly as possible, the premature melting of the mass being as far as possible prevented by frequent stirring. However, as the temperature soon rises above 392° F., partial fusion can no longer be prevented, and the mass becomes moist and crummy. Heating is continued for 1 to 1½ hours, the temperature being only gradually allowed to rise to 494° F.

As shown by the table given above, a mixture of 40 parts of caustic potash and 60 parts of caustic soda gives exactly the same yield of oxalic acid as pure caustic potash by itself, but the price of the latter being much higher than that of caustic soda, it will be of advantage to use in practice the two alkalies in the proportion given above.

The turbulent reaction during fusion may, it is claimed, be prevented, so that the preparation of oxalic acid takes place quietly and smoothly, by adding to the mixture of sawdust and alkalies heavy hydrocarbons, for instance, machine oil or vaseline oil, and, according to Capitaines and Hertlings, who have patented a process for this purpose, the use of caustic soda by itself suffices for the formation of abundant quantities of oxalic acid. They use a soda lye of 1.35 specific gravity in the proportions of 40 parts of sodium hydroxide to 20 parts of sawdust and 1.5 parts of hydrocarbon combinations. The temperature need not exceed 392° F., and the resulting yield of oxalic acid is claimed to amount to 140 parts for every 100 parts of wood.

PREPARATION OF OXALIC ACID ON A LARGE SCALE.

With the use of the process introduced by Thorn, the preparation of oxalic acid is divided into the following operations:

Preparation of the mixed caustic lyes and their concentration by evaporation to a specific gravity of 1.35.

Mixing the lye with the sawdust and heating the mixture to the maximum temperature to be used.

Production of sodium oxalate from the melt, conversion of it into calcium oxalate, and separation of the oxalic acid from the latter; recrystallization of the crude oxalic acid.

In preparing the mixed lyes the content of pure potassium carbonate and sodium carbonate in the potash and soda to be used has first to be determined, and the two salts must be mixed in such a proportion that the lye contains exactly 40 parts of caustic potash and caustic soda. The solution of the salts is made caustic in the usual manner by means of quicklime, and evaporated in iron pans to 1.35 specific gravity. It is then immediately mixed with the sawdust in the proportion of 1 part of the latter to 2 parts of alkali.

MELTING APPARATUS.

The apparatus for heating the mass to the maximum temperature required for the formation of oxalic acid must be of such a nature that the temperature of the mass can be readily regulated, and that the workmen are completely protected from the vapors evolved from the mass during heating. These vapors have a troublesome effect upon the respiratory organs and eyes, and provision for their immediate removal has therefore to be made. This may be effected by placing over the plates upon which heating takes place, a jacket extending down as far as possible without impeding the work. The jacket terminates above in a shaft in which a very strong current of air is produced by a steam ejector or a fan. In this manner the vapors arising

from the plates are immediately carried away and blown into a high chimney or, still better, under the grate of a fireplace.

Since in heating the mass the temperature must not exceed 494° F., it would seem advisable to effect heating the plates by means of a current of hot air or superheated steam, the use of an iron box 4 to 6 inches deep and 6½ feet long and wide being most suitable for the purpose. On the front of the box, *i. e.*, the side turned towards the workmen, is a pipe through which the heated air or superheated steam passes into the box, the pipe being furnished with a stopcock, by means of which heating can be regulated as desired.

To prevent the mass spread out upon the surface of the box from acquiring in some places too high a temperature, it has to be frequently turned, and it is advisable not to use for this purpose iron hand-rakes, but to employ a mechanical contrivance similar to that used in malt-houses for turning the malt in the kiln. Such a contrivance can be run by a small motor so that the entire attention of the workmen is directed towards the mass in hand.

The mass having been spread out upon the iron plate in a somewhat thicker layer than is possible without the use of a mechanical turning contrivance, a full current of steam or hot air is immediately admitted for the purpose of rapidly heating it and evaporating the water still adhering to it. To prevent caking, the turning apparatus is at once set to work.

The temperature may now in a short time be brought to 392° or 410° F., and then gradually raised to 464° or 473° F. At this temperature the mass is kept for from one to one and a half hours, the admission of steam or hot air being so regulated that the temperature cannot rise any higher. The mass is now considered finished and removed from the heating apparatus by means of iron rakes.

WORKING UP THE MELT.

The mass contains all the sodium held by it fixed to oxalic acid; in addition it contains potassium carbonate and humus substances which give it a quite dark coloration. The mass is immediately thrown into a vessel containing a certain quantity of water, which is in a short time brought to boiling, and in this state rapidly dissolves the sodium oxalate. It is advisable to place in the vessel a steam coil to be able to directly heat the fluid. Only enough water is used for the boiling fluid to show a density of 35° Bé. The boiling fluid is allowed to run through a filter of close linen into a vessel in which, under constant stirring, it is rapidly cooled to the ordinary temperature.

Sodium oxalate dissolves with ease only in boiling water, it being but slightly soluble in cold water and, hence, by rapid cooling, a pasty mass consisting of very small crystals of quite pure sodium oxalate is obtained. This pasty mass is treated in a centrifugal for the removal of the mother-lye adhering to the crystals.

In addition to a very small quantity of sodium oxalate, the mother-lye contains the total quantity of the potash used in the form of potassium carbonate, and the humus substances which have been formed by heating the mass. The mother-lye is utilized by converting the potassium carbonate into caustic potash by means of quick-lime, and using it for the next operation.

However, in the course of several operations, the humus substances accumulate to such an extent in the mother-lye as to render it inadvisable to make it again caustic. It is then utilized for obtaining pure potassium carbonate, this being effected by mixing it with a sufficient quantity of sawdust to make a mass which can be taken up with shovels. This mass is burnt in a small reverberatory furnace, and the residue of ash calcined until white. It then consists of almost pure potash which may be used for further operations.

For the purpose of obtaining pure oxalic acid from the crude sodium oxalate, the oxalic acid is first fixed to lime, and the resulting calcium oxalate, which dissolves with difficulty, is decomposed by sulphuric acid, a solution of the oxalic acid being thereby obtained.

This operation is carried on by dissolving the crude sodium oxalate in boiling water in a vat furnished with a stirrer which is kept in constant motion. Milk of lime is then added to the boiling solution, whereby calcium oxalate, which dissolves with difficulty, and free caustic soda are formed. During the precipitation of the calcium oxalate, the fluid has to be constantly kept near the boiling point, as only under this condition, the precipitate turns out granular and settles rapidly on the bottom.

A sample is from time to time taken from the vat, filtered, acidified first with an excess of acetic acid, and then solution of calcium chloride is added. If the sample still gives a precipitate it is an indication that the total quantity of the sodium oxalate has not been decomposed and more milk of lime has to be carefully added. When the sample shows that decomposition is complete, the stirrer is stopped, the precipitate allowed to settle, and the supernatant caustic lye is drawn off. The precipitate is then several times washed with water, and the wash-waters are combined with caustic lye first drawn off. The total quantity of fluid thus obtained is evaporated in iron pans until the soda lye shows a specific gravity of 1.35, and can then be utilized for working fresh quantities of sawdust.

The calcium oxalate having been sufficiently washed is brought into a lead-lined vessel upon the bottom of which rests a steam coil, and mixed with a sufficient quantity of water to form a thin paste. While steam is being introduced through the narrow apertures with which the steam coil is furnished, dilute sulphuric acid (of 15° to 20° Bé) is allowed to run in. The quantity of sulphuric acid required can be approximately calculated, but in order to separate

all the oxalic acid and, at the same time, have no excess of sulphuric acid in the fluid, a sample of the latter has from time to time be tested. This is effected by bringing a small quantity of the white precipitate separated, which is to consist of gypsum, upon a filter, washing quickly with water, and then treating the mass with a small quantity of sulphuric acid. The filtrate now obtained is mixed with solution of potassium permanganate. If undecomposed calcium oxalate is still present in the vat, the fluid, which immediately after the addition of the potassium permanganate appears red, becomes discolored by the decomposition of the latter. If the fluid remains red, decomposition of the calcium oxalate is complete.

PRODUCTION OF PURE OXALIC ACID.

The vat now contains a solution of oxalic acid in water standing over the precipitate consisting of calcium sulphate. The solution is drawn off, the precipitate is several times washed with water to obtain the last traces of oxalic acid, and the oxalic acid solution is finally highly concentrated by evaporation, the latter being effected in pans very similar to those used for evaporating solutions in the manufacture of tartaric acid. The pans consist of large, shallow, lead-lined wooden boxes, furnished with a lead heating coil. Two such evaporating pans are placed one above the other so that the contents of the one placed at a higher level can be discharged into the lower pan.

The oxalic acid solution is first brought into the upper pan and evaporated to a density of 15° Bé. It is then allowed to cool and run into the lower pan. The reason for this interruption of the evaporation is that the dilute solution of oxalic acid contains quite a large quantity of gypsum in solution, and the latter separates completely only when the fluid has acquired the above-mentioned concentration. After removing the precipitated gypsum from the bottom of the pan, the latter is again charged with

crude oxalic acid solution. The solution in the lower pan is evaporated to 30° Bé., and then left to crystallize either in large stoneware dishes or in lead-lined vats. It is advisable repeatedly to stir the fluid during cooling, small crystals which include but little mother-lye being thereby obtained.

When the fluid in the crystallizing vessels has become entirely cold, the crystals are freed as far as possible from mother-lye by treatment in a lead-lined centrifugal, the crystals of crude oxalic acid thus obtained being available for many technical purposes as their slightly brownish color is not objectionable.

An almost chemically pure product is produced from the crude oxalic acid by dissolving the latter in the smallest possible quantity of boiling water, and stirring into the hot solution a small quantity of finely-powdered animal charcoal. The fluid is then allowed to stand until the animal charcoal powder has settled on the bottom of the vessel, and the at first brownish fluid has become as clear as water. The hot solution is then allowed to run in a thin stream into the crystallizing vessel and the resulting crystals are completely dried by whirling in a centrifugal. The oxalic acid thus purified contains neither free sulphuric acid nor calcium oxalate, and may be considered a highly refined article.

The mother-lye obtained by the first treatment of the crystals of crude oxalic acid in the centrifugal contains considerable quantities of free sulphuric acid, and the latter is made use of by employing the mother-lye in the next operation of decomposing the calcium oxalate, a smaller quantity of sulphuric acid being of course then required.

VII.

VISCOSE AND VISCOID.

The products to which these terms have been applied, were first prepared, in 1892, by Bevan, Beadle and Cross. With reference to their properties it may be expected that in the course of time, they will find extended application in the industries, because from them can be prepared cellulose in a perfectly pure state in the form of completely homogeneous masses of any desired size, and it is possible to color them, or mix them with a solid body so that a plastic mass is obtained, the nature of which allows of the most diverse technical applications.

The main point of the invention lies in the fact that a combination of cellulose and soda forms, on addition of carbon disulphide, a substance, the solution of which is called viscose on account of its uncommon viscosity. When such a soda-cellulose-carbon disulphide solution is exposed to the air, a gradual disintegration of the combination takes place, the carbon disulphide evaporating and, in many cases, sulphuretted hydrogen also escaping from the mass. The latter becomes constantly of greater consistence, and when all the carbon disulphide has finally evaporated, pure cellulose intermingled with soda, which, however, can be readily removed by washing, remains behind. To the cellulose thus obtained the term *viscoid* is applied. By exposure to a higher temperature the viscose solution is in a very short time decomposed.

The progress of the conversion of viscose into viscoid can be regulated at will by the use of a suitable temperature, and during this time coloring-matter or any desired pulver-

ulent bodies may be incorporated with the mass, which becomes constantly more thickly fluid, so that at the end of the operation a body is obtained resembling, as regards its properties, wood, horn or stone.

If no additions are made, there is finally obtained pure cellulose in the form of a white mass, which in thin layers is, however, perfectly colorless, and this also allows of an entire series of special applications. A few masses which can be prepared from viscoid will later on be more closely described.

The process for the preparation of viscose has been modified by several technologists, but the main point remains the same in all the methods, namely, that soda-cellulose is first prepared and then converted by the addition of carbon disulphide into viscoid, which is dissolved in water.

Cellulose of various derivatives is used as raw material for the preparation of the viscose solution. Purified cotton may be employed just as well as cellulose obtained from wood, and cleaned scraps of cotton and linen fabrics may also be utilized. In paper mills, viscose is especially employed for sizing finer qualities of paper, and for its preparation so-called half-stuff, prepared from cotton and linen rags, is frequently employed, as well as waste-paper which must, however, be entirely free from wood-pulp.

PREPARATION OF VISCOSE.

For experiments on a smaller scale in the preparation of viscose, it is best to use as basis-materials purified cotton or paper free from mechanical wood-pulp, because in working other materials, the assistance of disintegrating and mixing machinery is indispensable, while the above-mentioned materials can be readily converted into soda-cellulose, and the latter into viscose.

For working on a small scale, the cotton or paper is brought into a large rubbing dish and concentrated soda lye poured over it, the latter being distributed as uniformly

as possible throughout the mass by means of a pestle. Enough soda lye is gradually added so that for about two parts by weight of dry cellulose, one part by weight of caustic soda is used, and the mixture when finished contains in round figures, six parts of water. When the entire quantity of caustic soda has been added, the dish is covered and allowed to stand for some time so that any fibres which may not have been moistened, can come in contact with the caustic soda. The mass consisting of soda-cellulose is then quickly pressed out, brought into a flask and 40 per cent. of its weight of carbon disulphide poured over it. The mass soon becomes transparent and gelatinous without, however, becoming fluid, its viscosity being so great that it liquefies only when a sufficient quantity of water is added. By allowing the flask to stand quietly, the particles which have remained undissolved, settle gradually on the bottom, and the supernatant fluid of a yellowish color becomes almost entirely clear. This fluid consists of a solution of viscose in water.

If a layer of this solution be uniformly distributed upon a glass plate—in the manner photographers do with collodion—it becomes in a short time gelatinous and finally solid and odorless. If now the glass plate be placed in water, changing the latter several times, the soda is dissolved and, after drying, a perfectly colorless film of structureless cellulose can be drawn off from the glass plate. By mixing certain quantities of viscose solution with coloring substances or pulverulent bodies, experiments on a small scale may also be made for the production of masses with fixed properties.

PREPARATION OF VISCOSE ON A LARGE SCALE.

For the preparation of viscose on a large scale, such cellulose as is made for paper-manufacturing purposes is generally used, a short-fibered product with fibres 0.059, or at the utmost 0.079, inch in length being generally selected,

because experience has shown that long-fibered cellulose requires a much longer time for conversion into soda-cellulose. Since the process proceeds in a correct manner only when the soda lye shows a certain degree of concentration, the cellulose should contain only a limited amount of water, not exceeding 50 per cent. Hence the content of water in the cellulose has to be accurately established, the quantities of further additions being determined thereby.

The operation commences with the comminution of the cellulose. Small disintegrators were formerly used for this purpose, but at the present time the cellulose is worked in the same manner as for blotting paper, the knife of the hollander being so set as to obtain a product of as short a fibre as possible. The mass coming from the hollander is as far as possible freed from water in a centrifugal, and is then spread out in layers and left until it is air-dry.

The quantitative proportions between cellulose and caustic soda used in practice vary within very wide limits. The use of more caustic soda than is absolutely necessary for the formation of soda-cellulose being mere waste, the quantity required for every fresh batch of cellulose should be accurately determined by an experiment on a small scale, because in working many hundred pounds of cellulose one-half per cent. more or less of caustic soda represents a considerable sum.

The proportions generally used are as follows: Air-dry cellulose, 25 to 33 parts; caustic soda, 12.5 to 16; water, 52 to 55.

The caustic soda, which should always be used in the form of a concentrated solution, is mixed with the cellulose, water being gradually added, because the at first highly concentrated soda solution acts more rapidly than when the entire quantity of water is at once used. It may here be remarked that the quantity of water given above includes the water contained in the air-dry cellulose.

The commencement of the formation of soda-cellulose is

recognized by the behavior of the mass, it swelling up very much, and a considerable increase in the temperature also takes place. When the mass has acquired the appearance of crumbled bread it is an indication that the process is finished.

In practice the preparation of soda-cellulose is effected by two different methods, and every manufacturer, after having once adopted one of them, prefers it to the other. However, both are perhaps of equal value, and experience and practice play no doubt an important part in obtaining a product of suitable properties. According to one of the methods the cellulose is from the start worked with soda lye of the proper degree of concentration, while according to the other, an excess of soda lye is used, which later on is removed.

In working according to the first process, the cellulose is treated in a mill, similar in construction to a rag-engine used in the manufacture of paper for breaking up half-stuff. The cellulose is first for a few minutes worked by itself for the purpose of loosening it, and the soda lye is then allowed to run in in small portions at a time, a fresh quantity being only added when the first portion has been absorbed. If too much soda lye were at one time added the mass would become very slippery, and the runner of the mill would slide, instead of rolling, over it.

When the total quantity of soda lye has been added the mill is kept in motion until the termination of the process is indicated by the mass becoming crummy. Since the mass may contain harder lumps, which might cause the formation of a non-homogeneous product, it is passed, after being taken from the mill, through a sieve with meshes not over 0.19 to 0.23 inch wide. The sifted mass is immediately brought into the storage vessels, which must be closed air-tight, though it may also be at once used for the preparation of viscose.

For the preparation of soda-cellulose according to the other method, in which soda lye in excess is used, the cellu-

lose is first mixed with about ten times the quantity of soda lye of 15 to 18 per cent. The lye is allowed to act until the operation is finished, the portion of it which has not been absorbed is discharged, and the mass is treated in a centrifugal, a certain quantity of lye being thereby regained. By simply mixing the cellulose with the soda lye, lumps are frequently formed in the mass in consequence of the increase in volume which takes place, and the soda-cellulose after coming from the centrifugal has to be especially comminuted and passed through a sieve.

SODA-CELLULOSE.

In storing soda-cellulose prepared according to one of the processes described above, it will sometimes be observed that it becomes heated to quite a high degree. This phenomenon can only be explained by assuming that the formation of soda-cellulose is only incompletely effected in the apparatus used for the purpose, and that it is gradually effected in the storage vessels. However, by this process a certain quantity of heat is liberated, which by reason of the wood of the barrels used for storage being a bad conductor, is kept together.

Since the quality of the soda-cellulose is impaired by this development of heat, and there may be even danger of a fire breaking out in consequence of it, certain precautions, given below, should be observed in storing soda-cellulose.

The main point in the manufacture of soda-cellulose is to have the entire process finished as rapidly as possible, soda-cellulose being a body which absorbs with avidity carbonic acid from the air, and to bring the product immediately into the storage vessels, closing the latter air-tight.

STORING SODA-CELLULOSE.

Soda-cellulose being a combination of but slight constancy, only such a quantity should, as a rule, be prepared in one operation as can be worked into viscose in three or

four days, experience having shown that a very thickly-fluid viscose cannot be obtained from soda-cellulose which has undergone changes by long storing, the product in this case possessing but little viscosity.

The injurious changes soda-cellulose undergoes appear the more quickly the higher the temperature is to which it is exposed. Hence means should be provided in every factory by which the product can be kept in an unchanged state from the moment it leaves the mill and has been passed through the sieve. Instead of bringing the product into a wooden vessel, it is allowed to fall into a large sheet-iron vessel which is surrounded with ice. When this vessel has been filled with the sifted mass, a thermometer is pushed into the center of the latter, and the vessel closed with a well-fitting lid. Soda-cellulose being a bad conductor of heat, some time is required for the mass to cool throughout, and it must be allowed to stand until the thermometer indicates a temperature of 41° to 43° F. The mass is then quickly packed into the storage barrels and the latter are placed in a cool cellar, best in an ice-house. The expense of the ice required is slight in comparison to the loss incurred by the spoiling of a quantity of the product. In storing the soda-cellulose at such a low temperature larger vessels may also be used. However, in storing the product at a higher temperature, the use of smaller barrels of about 220 lbs. capacity would at all events appear not advisable, since, as is well known, the heat from the outside acts more rapidly in a smaller vessel than in a larger receptacle.

Comparative experiments have shown that soda-cellulose stored in an ice-house remained unchanged after two months, but its stability decreased with every degree of heat. A maximum temperature of 50° to 53.6° F. would appear to be most suitable for the storage room, and if artificial cooling is not to be applied, the cold season of the year is best adapted for the manufacture of soda-cellulose.

However, in many countries the manufacturer is, even in the cold season, subject to the caprices of the weather, and it is therefore advisable to combine a cooling plant with a viscose factory. Soda-cellulose, which was kept at 68° F.—the ordinary temperature of a room—became, as a rule, so changed in 60 to 70 hours that it could no longer be used.

As regards the products formed by the decomposition of soda-cellulose in consequence of the action of too high a temperature, the appearance of acetic acid (formic acid?), lactic acid and acetyl-lactic acid has been established. These combinations, however, can only appear with the complete decomposition of the cellulose. Hence it appears probable that the alteration of the soda-cellulose commences with a transposition inside the molecule of the cellulose, the consequence being that a large part of the substance is no longer soda-cellulose, and hence cannot form the combination to which the term viscose has been applied.

The unpleasant observations made in working soda-cellulose in which alteration has already commenced are of varying nature, but the fluid lacks chiefly the great viscosity and adhesive power which are its characteristic properties. The cellulose recovered from such a thin solution possesses but little strength, and is so brittle that it can scarcely be worked.

PREPARATION OF VISCOSE.

Viscose is formed by simply bringing together at the ordinary temperature soda-cellulose with carbon disulphide, the process taking place the more rapidly the more intimate the contact between the two bodies. Chemically the combination formed is cellulose sulphocarbonate. It is readily soluble in water and on exposure to the air is decomposed at the ordinary temperature, cellulose in the form of a colorless and structureless mass being separated. At a higher temperature decomposition progresses with great rapidity.

In preparing viscose it must be borne in mind that car-

bon disulphide is a very volatile substance—its boiling point being at 118.4° F.—and vessels which can be closed absolutely air-tight have to be used. Carbon disulphide frequently contains small quantities of sulphur in solution and as this would have an injurious effect upon metallic vessels, apparatus entirely constructed of wood should be employed.

The most suitable, and at the same time the most simple, apparatus for the preparation of larger quantities of viscose is a revolving barrel with quite a large bung-hole, which can be securely closed with a screw-cover. In place of a revolving barrel, a stationary barrel may also be used. The contents are mixed by means of a stirrer consisting of a shaft with shovel-like paddles with which the barrel is furnished.

The proportion between soda lye and carbon disulphide is, by the way, 10 to 1. For 100 parts of soda-cellulose 10 parts of carbon disulphide are used, though a small excess of the latter is of no importance. When both the substances have been brought into the apparatus, the latter is securely closed and set in motion, being thus kept uninterruptedly until the formation of the combination is com plete. The time necessary for this purpose depends largely on the temperature; three hours being, as a rule, required with a temperature of 60° F., while with one of 77° to 86° F., the formation of the combination may be complete in one hour.

The cellulose sulphocarbonate forms a loose mass, differing in appearance from soda-cellulose only by its pale yellow color. When brought in contact with water it should gradually be completely dissolved. If any flakes remain undissolved, it may be due to two causes, one of them being that all the cellulose has not been converted into soda-cellulose, and the other, that an insufficient quantity of carbon disulphide has been used, or that it has acted for too short a time. In the first case, the mass cannot be im-

proved, but, in the second, an experiment may be made by continuing the manipulation in the revolving barrel with the addition of a certain quantity of carbon disulphide.

When the proportions have been correctly chosen, a small excess of carbon disulphide remains, as a rule, behind. This may be recovered by attaching to the hollow shaft of the barrel a pipe ending in a coil which terminates in a vessel filled with ice. A small suction pipe is placed on the lower end of this ice vessel. The other end of the hollow shaft of the revolving barrel is furnished with a small cock. This cock is opened and the suction pump set in motion while the barrel is slowly revolving, a current of air being thus sucked through the contents of the barrel whereby the excess of carbon disulphide is evaporated. The vapors on coming in contact with the ice are condensed, and ice water and carbon disulphide run off into a collecting vessel placed at the lower end of the ice-holder.

PREPARATION OF VISCOSE SOLUTION.

For this purpose the contents of the revolving barrel are brought into a closed vessel which is furnished with a vigorously-acting stirring contrivance, and, after setting the latter in motion, water in small quantities is allowed to run in. Immediately after the first portions of water have been admitted, the mass commences to swell up very much, and would in a short time acquire such a degree of viscosity as to impede the motion of the stirrer. Hence more water is allowed to run in until the quantity of it admitted amounts to $1\frac{1}{2}$ times the weight of the soda-cellulose brought into the apparatus.

The stirrer is kept in motion until solution is complete, when the viscose is immediately brought into the vessels in which it is to be stored or shipped. Viscose should as far as possible be protected from the access of air, being rapidly decomposed on coming in contact with it. Viscose solution which is immediately to be used in factories where

it has been prepared, may be kept in an open vessel of wood or zinc-sheet. A layer of water is carefully poured upon it so that no mixing of the two fluids takes place; this layer of water protecting the viscose from becoming decomposed. When viscose solution is allowed to stand open, a thin film of cellulose forms in a short time on the surface, and this has to be removed when the viscose is to be used.

STORING VISCOSE.

Since viscose is rapidly decomposed by the access of air, as well as at a higher temperature, special precautionary measures have to be taken to prevent decomposition when larger quantities of it are to be stored. As is the case with soda-cellulose, these precautionary measures consist in shutting out the access of air, and keeping the storage-room at a low temperature.

The most simple plan is to store the viscose in a sheet-zinc cylinder provided around its upper edge with a gutter, into which fits the $1\frac{1}{2}$ to 2 inches deep rim of a sheet-zinc lid. The vessel having been filled, the lid is placed in the gutter and the latter filled with water, thus forming a kind of hydraulic joint, which renders the access of air to the contents of the cylinder impossible.

The stability of the viscose is the greater the lower the temperature of the room in which it is stored. In rooms having a temperature of 77° F. or more, decomposition takes place very rapidly; at the ordinary temperature of a room viscose cannot be kept longer than 5 or 6 days without undergoing a change, and stability for two weeks can only be counted upon with a temperature below 50° F.

If, however, viscose solutions are stored in a room the temperature of which is kept, by artificial cooling, not much above the freezing point of water, the viscose can be kept in a perfectly unchanged state for a number of weeks. Independent of the assurance of preserving the viscose in an unchanged state, storing it at a low temperature offers a

great advantage in working the material. The temperature of the viscose when taken from the storage vessel is of course quite low, and as it becomes gradually higher in the normal warmth of the work-room, there is no difficulty whatever in working it at the degree of heat best adapted for the work in hand.

The shipping of viscose, especially during the warm season of the year, is connected with many difficulties, which can only be overcome by special precautionary measures. Viscose is shipped in closed sheet-zinc vessels, and when the latter are in a hot summer day forwarded by railroad, there is great danger as regards the stability of the product, since the temperature of freight cars exposed to the sun frequently reaches 95° F. or more. Hence the viscose, cooled down to a low temperature, should be shipped by fast freight, and the vessels containing it be protected as much as possible from heating by wrapping them in wet cloths.

PROPERTIES OF VISCOSE SOLUTIONS.

The commencement of the decomposition of a viscose solution is first of all recognized by the mass, at first only viscid and of about the consistency of a gum solution, becoming thicker and acquiring the consistency of a warm glue solution at the beginning of coagulation. As decomposition progresses the mass assumes the consistency of jelly. By taking it in hand at the right time, the mass may be restored to a useful condition by adding a suitable quantity of water, thus making it again more thinly-fluid.

It is probable that changes constantly take place even in a perfectly available viscose solution, as shown by the behavior of viscose when exposed in a thin layer to the air. In many cases decomposition simply takes place by vapors of carbon disulphide escaping from the mass, which constantly becomes more thickly-fluid, and finally nothing but cellulose remains behind.

In other cases it will, however, be noticed that sulphur-

etted hydrogen is evolved, and that the mass contains considerable quantities of sodium carbonate as well as sulphides and trithiocarbonate. The appearance of these combinations can only be explained by the decomposition, by the action of the alkali, of a portion of the carbon disulphide present.

The decomposition of the viscose is very much influenced by the temperature at which it takes place. Viscose solution exposed upon a glass plate to a temperature of but a few degrees above the freezing point is changed very slowly; the mass constantly acquires greater consistence and a solid, structureless film consisting of cellulose remains finally behind. The higher the temperature, the shorter the time in which decomposition takes place and at 104° F., it proceeds with great rapidity. When the temperature rises above 122° F., a homogeneous, coherent mass is no longer obtained, but one which here and there shows white spots which are produced by numerous small bubbles. At this high temperature decomposition takes place with such rapidity that the vapors evolved can no longer escape from the mass on account of its viscosity, but are retained in it like air-bubbles in rapidly freezing ice. At a still higher temperature, for instance, pouring the solution upon a highly heated plate, decomposition of the viscose takes place almost instantly, a mass of a very porous, spongy nature being obtained.

In many cases, for instance, in using viscose for sizing paper, it might be desirable for decomposition to take place more rapidly at the ordinary temperature than usually is the case, and this may be done by replacing the soda in the viscose by ammonia. The decomposition of viscose prepared in this manner takes place at a much lower temperature than that of soda-viscose, and carbon disulphide and ammonia escape in abundance from the decomposing mass. As previously mentioned, the behavior of viscose in decomposing depends on the temperature and its age, and

only by long, practical experience is it possible to judge from the start of its action in this respect. Hence to avoid disagreeable occurrences it is recommended to test a small quantity of every fresh viscose to be worked as to its behavior, and to arrange the course of the work accordingly.

CONVERSION OF VISCOSE INTO VISCOID.

When a 0.15- to 0.19-inch-deep layer of a viscose solution in a vessel is exposed to a temperature not exceeding 40° F., a thin film is first formed, and, by exercising care, can be lifted off. If this film be brought into water it redissolves, and therefore it consists evidently of a combination having some resemblance to viscose, though it appears in a solid form. If, however, this film be for some time exposed to the air it loses its solubility in water, but swells up in it to a jelly-like mass. If finally it be exposed for from half an hour to an hour to a temperature of 212° F., it has become entirely indifferent to water and behaves towards it like a film of nitro-cellulose.

Except for the production of very thin films and threads, viscose is seldom used by itself. For the preparation of thicker plates from viscoid—this term being applied to congealed viscose—a special method has to be adopted in order to obtain a perfect product. First of all it is necessary to know how thick the plates will be which can be obtained from a viscose layer of determined thickness by its conversion into viscoid, and this is ascertained by a preliminary experiment on a small scale. For the preparation of thick plates or blocks, sheet-zinc vessels of appropriate depth are used and filled with viscose. The vessels are then exposed in a room perfectly free from dust to a uniform temperature of 95° to 104° F. until the mass remaining in them has acquired the requisite quality. In order not to be inconvenienced by the vapors of carbon disulphide and other products of decomposition escaping from the mass, it is advisable to place the vessel in a box furnished with a pipe

entering a chimney, and to keep the temperature of the box uniformly at the above-mentioned degree, by a few heating pipes.

When a solid mass has been formed it is removed from the vessel and for some time heated at 212° F. Viscoid being a bad conductor, this heating must be continued the longer the thicker the plates are; at any rate it must be continued till the plates when dipped in water no longer swell up.

The plates are then laid in clean water, by which the salts contained in them are slowly dissolved, the water being renewed so long as soluble substances from the viscoid are absorbed by it. When the work has been carefully done the viscoid plates present the appearance of transparent glass. If the plates show here and there dull specks or white opaque spots, it is an indication of too high a temperature having been used in drying up the viscose, and that the mass is interspersed with small bubbles.

BEHAVIOR OF VISCOSE TOWARDS METALLIC SALTS.

When a viscose solution is brought together with a metallic salt, reciprocal decomposition takes place, the metallic oxide combining with the cellulose and the sulphocarbonate, while the soda fixes the acid of the metallic salt. The new combinations thus formed have not yet been sufficiently investigated as to their availability in practice, though a few of them have found practical application in the manufacture of paper. By mixing magnesium sulphate with viscose, magnesium-viscose and sodium sulphate are obtained, and as both these salts are readily soluble in water, no precipitation takes place after adding the magnesium sulphate. Magnesium-viscose possesses the property of decomposing with still greater rapidity than soda-viscose, which makes it very valuable for certain purposes, especially for sizing paper; the sodium sulphate adhering to the decomposed mass being a readily soluble salt can without trouble be removed from the paper mass.

By adding to a viscose solution the solution of a salt of a heavy metal, insoluble viscose of the metal added is formed. With the exception of the zinc combination, which is used for sizing in the manufacture of paper, none of these combinations has become of technical importance.

The proportional quantities of the bodies which are added to sodium-viscose for the purpose of obtaining other varieties of viscose, vary according to the object which the preparations in question are to serve. Thus, for instance, in paper mills 9 parts ammonium sulphate, or 15 parts magnesium sulphate, or 18 parts crystallized zinc sulphate are used for every 100 parts of a 10 per cent. soda-viscose.

PREPARATION OF VISCOSE ACCORDING TO CROSS.

According to a process recently patented by F. Cross, the quantity of caustic soda required for the preparation of viscose can be reduced one-half by treating the cellulose to be worked previous to submitting it to the action of the alkali, with dilute acids, at a temperature of between 212° and 284° F. This is of great advantage, because on the one hand, with the use of large quantities of caustic soda the cost of producing the article is considerably greater, and, on the other, the large content of alkali and sulphur in viscose prepared according to the older method is an impediment to its use for many purposes.

The preparation of cellulose according to this process may be effected in various ways. According to one method the fibrous cellulose is treated as follows: Paper pulp, half-stuff, rags, waste paper, etc., are for a few hours boiled with dilute (2 per cent.) hydrochloric or sulphuric acid; or the fluid is brought to the boiling point by itself when the cellulose is introduced, boiling being constantly kept up, and allowed to remain in the fluid until it has been converted into the brittle modification. According to another method, the cellulose is completely saturated at the ordinary temperature with dilute (2 per cent.) hydrochloric acid. The

excess of hydrochloric acid is then removed by treating the mass in a centrifugal, and the cellulose is completely dried at a temperature of between 140° and 176° F., care being taken that drying is uniformly effected. The transition of the cellulose to the brittle modification then takes place during drying.

According to a third method given by Cross, the cellulose is for a short time treated with dilute (1 per cent.) sulphuric acid in a digester under high pressure at a temperature of between 212° and 284° F. In place of dilute sulphuric acid, dilute hydrochloric acid containing but ½ per cent. of acid may also be used. The quantity of acid used should amount to five times the weight of the cellulose to be worked. The mass coming from the digester is freed from the acid fluid by washing, and pressed to reduce its content of water to between 50 and 40 per cent.

The most advantageous proportional quantities of caustic soda and water to be used for the cellulose thus prepared are within the following limits: Cellulose 40 to 50, caustic soda 10 to 12, water 50 to 38 per cent.

The soda lye is used in accordance with the content of water in the cellulose to be worked, and the further manipulation of mixing to soda-cellulose is generally effected in a crushing mill or other grinding contrivance, the operation being continued until the mass is perfectly homogeneous. The conversion of the soda-cellulose into viscose, and of the latter into viscoid, does not differ from the method previously described.

PREPARATION OF VISCOSE ACCORDING TO SEIDEL.

H. Seidel's process for the preparation of viscose differs but little from the one just described. According to the inventor's statements, 100 parts of sulphite-cellulose are for a few hours placed in dilute (1 per cent.) hydrochloric acid, the mass is then squeezed out and rinsed in water. It is then brought into intimate contact with a solution of

40 parts of caustic soda in 100 parts of water, and left to itself in a closed vessel for three days. One hundred parts of carbon disulphide are then brought into the vessel and distributed by stirring, when the mass is again allowed to repose for 12 hours. A yellow-colored solution is formed from which the viscose may be precipitated by alcohol or common salt solution.

Viscose prepared from sulphite-cellulose dissolves with somewhat greater difficulty, but has the advantage of being lighter in color than other varieties, and can even be obtained entirely colorless. It is less suitable for the preparation of plastic masses, but is remarkably well adapted for sizing paper.

According to Seidel, transparent plates of viscose are obtained from cotton by treating cotton fabrics, according to the process just given, up to the period at which the addition of carbon disulphide is to be made. Instead of adding the latter, the fabrics are hung in a room the atmosphere of which is saturated with carbon disulphide vapors, allowing them to remain for twelve hours. The rinsed fabric is stretched smoothly upon a glass plate, exposed for two days to the air, then completely dried in a drying closet, and finally placed in dilute hydrochloric or acetic acid.

According to this process, plates are obtained which have the appearance of parchment, and by heating to 212° F., become so plastic that they may be given any desired shape. They can be bleached with chloride of lime and then form a perfectly colorless mass, which, when colored, retains its transparency. It may here be remarked that the process above described would seem to be of but little practical importance since viscoid plates can be prepared in a much simpler, and at the same time cheaper, manner from ordinary viscose by spreading a somewhat thicker layer of the latter upon a glass plate provided with a rim of appropriate height, detaching the smooth plate from the glass plate, and treating it further in the usual way. The use of

cellulose in the form of cotton offers no advantage, but considerably increases the cost of production.

The process above described may, however, be utilized to advantage for giving a loosely-woven, thin tissue the appearance of a close and firm fabric. For this purpose the washed and dried tissue is unwrapped from a roll into a vessel containing the soda lye, remaining in it for several days so that a considerable quantity of soda-cellulose may be formed.

The tissue is then freed from the greater portion of adhering fluid by subjecting it to strong pressure between two rolls. It is next loosely hung up in a chamber, the door and windows of which can be closed air-tight. A shallow vessel filled with carbon disulphide is placed upon the floor of the chamber and the latter closed air-tight. The tissue is allowed to remain in the chamber until the quite dark yellow color it acquires by the action of the carbon disulphide remains constant.

The chamber is then opened, thoroughly aired and the tissue is removed when it has again become white and perfectly dry. It is then taken through a bath of dilute (2 to 3 per cent.) hydrochloric acid, washed and dried in a stretched state, this being necessary as otherwise it would shrink very much.

Tissues thus treated appear nearly twice as thick as originally, feel firm to the touch, and possess remarkable strength. These phenomena may be explained by the change the separate fibres of which each thread consists have undergone. Every fibre on its surface and to within a certain depth has been converted into viscose which penetrates the entire mass like varnish. The tissue taken from the carbon-disulphide chamber acquires, when moistened with water, a quality reminding one of a thoroughly soaked animal skin. When the viscose is again decomposed the separated cellulose cements the finest fibres of the threads most intimately together, and this explains the compact ap-

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pearance, firm feel, and great strength of the tissues thus treated.

PREPARATION OF CHEMICALLY-PURE CELLULOSE-SULPHO-CARBONATE (VISCOSE).

Viscose prepared according to the ordinary method is not a pure product consisting solely of the combination cellulose-sulphocarbonate, but always contains certain quantities of sodium carbonate, thiocarbonic acid and carbon disulphide. According to the process of the Viscose Syndicate Limited, it can be freed from these bodies by treating the raw product with weak acids—lactic, formic or acetic acid —in excess, whereby the viscose is not changed, but the above-mentioned foreign bodies are rendered harmless. The fluid is then mixed with a water-withdrawing body, such as alcohol or common salt solution, and entirely pure viscose which separates as a mass of leathery appearance, is thus obtained. The product is again washed with dilute alcohol or common salt solution, and dried.

Pure viscose obtained in the above-described manner, is a neutral, colorless and odorless mass, which rapidly dissolves in water without leaving a residue, and is especially well adapted for sizing paper and fabrics.

USES OF VISCOSE.

Viscose, or viscoid prepared from it, is already used to a considerable extent in various industries, and it may be supposed that both these substances will find various technical applications. Viscoid, as previously explained, is simply pure cellulose, and it being in a certain measure available in a fluid state in viscose, it is possible to obtain the cellulose in a solid form and to give the article thus obtained any desired color.

Quite bulky bodies can be prepared from viscose, and any desired pulverulent substances may be incorporated with the mass as it becomes solid, so that the articles pro-

duced in this manner resemble, as regards their appearance and partially their properties also, horn, ivory, wood or stone. In the same manner transparent plates or very thin leaves may be prepared from viscoid, or they may be obtained in the form of exceedingly fine threads well adapted for spinning.

From what has been said, it seems more than probable that viscose, as well as viscoid, may in the future strongly compete with celluloid, the cost of producing it being, on the one hand, less, and on the other, it is not nearly as inflammable as celluloid, the great combustibility of the latter requiring constant precaution in handling it.

It would be impossible to give a detailed description of all the uses to which viscose and viscoid might be applied. However, the suggestions made here will be sufficient to guide the practical man in the preparation of masses with determined properties.

USE OF VISCOSE IN THE MANUFACTURE OF PAPER.

Since by the decomposition of viscose there remains behind a substance consisting of a product, which has to be designated as paper in the actual sense of the word, no better sizing-agent for paper can be imagined. In view of the good qualities of paper sized with it, the use of viscose for this purpose has been widely adopted in the manufacture of paper, and large quantities of it are used.

Although soda-viscose may be directly used for sizing paper, it is at present employed only in exceptional cases, the removal of the considerable quantities of alkaline salts which pass into the paper mass being an unpleasant operation.

In place of soda-viscose, ammonium viscose, and the previously-mentioned compounds of viscose with magnesium or zinc, are at present used, these combinations possessing the advantage of decomposing still more rapidly than soda-viscose. In addition to cellulose, ammonium viscose and

magnesium viscose in decomposing yield throughout combinations soluble in water, which can be readily removed by washing from the paper mass. Furthermore, in the decomposition of these varieties of viscose, a far less abundant separation of carbon disulphide takes place than is the case with soda-viscose, as well as with zinc-viscose. A further advantage of the use of ammonium or magnesium viscose, as well as of zinc-viscose, is that a much smaller quantity of alum is consumed than is otherwise the case.

Papers prepared with viscose are distinguished by a firmer feel and besides, by the addition of this substance, great strength and extensibility are imparted to them.

Viscose may be applied to all kinds of paper, to the coarsest qualities of wrapping paper as well as the finest varieties of writing paper.

As shown by exact experiments, excellent results have been obtained by the application of viscose as a size to wrapping paper of which considerable strength is demanded, the breaking length as well as the elongation being increased 30 to 50 per cent.

Thorough experiments in this respect have been made by the Versuchsanstalt at Charlottenburg, and the figures given below show plainly how the qualities of the papers are affected by an addition of viscose:

Variety of paper.	Breaking length in meters.	Elongation in per cent.
Brown wrapping paper from steamed wood	3575	1.80
Same, sized with 4 per cent. of viscose	4750	3.00
Brown wrapping paper from steamed wood	3200	0.90
Same, sized with 4 per cent. of viscose	4650	2.40
Brown wrapping paper from steamed wood	2225	1.40
Same, sized with 4 per cent. of viscose	2925	1.97

If fine qualities of paper, the beautiful, pure-white color of which is of importance, are to be sized with viscose, care

must be taken to use a product of a very light color, otherwise the paper acquires a very noticeable yellowish tinge.

VISCOSE IN THE MANUFACTURE OF WALL PAPER.

In a similar manner as in cloth printing, viscose may be directly used in the manufacture of wall paper as a thickening agent for the printing colors employed for producing the designs upon the wall paper. As compared with the ordinary thickening agents, viscose has the advantage that the colors printed with it adhere far more firmly to the paper than is the case with other colors which frequently stick so badly as to be effaced by slight rubbing.

The use of viscose is of special advantage in the manufacture of the so-called flock paper, which is made by sifting upon sized spots of the wall paper finely comminuted colored wool and, after drying, removing the excess of wool dust. From most of the flock papers the larger portion of the wool can be readily removed by vigorous rubbing with a brush, but if the paper be printed with viscose and immediately covered with wool dust, the latter cannot be removed. Metallic bronze, aluminium powder, etc., triturated with viscose to a printing color and printed upon the paper, look like gilding and silvering and retain for years their metallic appearance.

Even wall paper, made in the ordinary way, if coated, when finished, with viscose solution acquires thereby the beautiful lustre characteristic to pure cellulose, and besides, it may be cleansed with a sponge moistened with water, solution of soap or soda without damage to its beautiful appearance. Wall paper which in the course of time has suffered from smoke and dust may by this treatment be restored to its original beauty. Washing may be repeated as often as desired, because the thin layer of cellulose upon the paper is perfectly water-proof and indifferent towards water and soap.

Imitations of leather and velvet hangings can in no

other way be made so beautiful and durable as with the use of viscose. By printing with viscose upon leather-brown paper, gold or silver bronze, and then coating its entire surface with viscose, it can, while still moist, be provided with raised or depressed designs so that in appearance the finished wall-paper cannot be distinguished from genuine leather hangings.

By printing designs of a certain form upon different places of the paper and covering them with wool powder of an appropriate color, then printing other places with viscose covering them also with different-colored wool powder, and thus continuing the operation, wall paper may be produced having the appearance of velvet hangings of a determined ground color with variously-colored flowers, leaves, ornaments, etc., woven in. It is advisable to pass wall paper made in this manner with the lower non-printed surface down, over a heated roll with such rapidity that the viscose layer is during a few seconds heated to 212° F. By this heating the viscose becomes perfectly insoluble and the wall paper can without risk be rolled up.

The examples given above suffice to show the important role viscose is likely to play in the manufacture of wall paper.

VISCOSE IN CLOTH-PRINTING.

In cloth-printing viscose may be used in various ways, namely, as a so-called resist and as a thickening and fixing agent for certain coloring matters. If a tissue of sheep's wool or silk be printed with various-colored designs by means of a viscose solution of appropriate strength, and the tissue be then passed over hot rolls, the proper places will be covered and impregnated with cellulose. The tissue may then be dyed in a dye-bath which yields its coloring matter to wool and silk, but not to cellulose, the result being a tissue showing a white design upon a colored ground.

If the printing color be prepared by stirring the finely pulverized coloring matter into thick viscose solution and the tissue be printed with it, it is only necessary for fixing the color in the most durable manner, to pass the printed tissue over heated rolls, the color being then imbedded in a layer of cellulose and cannot be removed.

Viscose solution can to great advantage be used for marking fabrics in mills, as well as a substitute for ink for marking household linen, etc. For this purpose a viscose solution sufficiently thickly-fluid to yield sharp impressions with a rubber stamp is used, a durable coloring matter being incorporated with it, finely-divided carbon in the form of lamp-black being most suitable as it is not dissolved by any known body. The tissues are marked with the assistance of the rubber stamp and after drying in the air, the color is fixed by passing a hot flat-iron over the mark. The carbon is then enclosed by cellulose, and the color is not only upon the surface of the tissue but has penetrated it throughout and is, therefore, indestructible. Even an attempt to dissolve the layer of cellulose enclosing the carbon, by treatment with cuprammonium solution, would result only in making the marking somewhat paler and less distinct, but it would be impossible to destroy it entirely, the particles of carbon adhering so tenaciously to the individual fibres of the tissue that they cannot be removed.

In place of carbon any desired pulverulent coloring matter may be used, but care must be taken that it is of such a nature as not to be changed by free alkali or carbon disulphide.

VISCOSE AS A SIZE OR DRESSING.

The size or dressing generally used in the textile industry consists, as a rule, of gum-like substances, a paste prepared from various kinds of starch being partially employed for the purpose. However, these agents are entirely removed by washing the fabrics once or at the utmost twice, and the

latter lose their good appearance and firm feel; as well as the lustre given to them by the size or dressing.

In addition the weight of the fabric is considerably decreased, because the pipe clay or heavy spar which had been added as a loading agent to the size, has also been washed out.

Viscose offers a means of sizing tissues in such a manner that they retain, even after repeated washing, their smoothness and lustre, and lose nothing in body. Sizing with viscose is effected in various ways according to the object which is to be attained.

The simplest mode of sizing consists in drawing the tissue from a drum upon which it has been wrapped and passing it through a vat filled with viscose solution of suitable concentration. By passing the wet tissue between two rubber rolls set close together, fixed above the vat, the excess of fluid is removed and falls back into the vat. After drying, the tissue appears sized with a layer of viscoid, the thickness of which depends on the concentration of the viscose solution used. By passing the tissue again through the viscose solution and repeating the operation, under special conditions, for the third time, sizing is finally effected to such an extent that all the pores of the tissue are closed with cellulose, and it is just as water-proof as if it had been impregnated with rubber.

Loading agents may also be added to the viscose, thus imparting great weight to the tissue, which it, however, retains when washed, because the particles of the loading agent are cemented one to the other, as well as to the fibres of the tissue, by the insoluble cellulose.

To impart to the tissue treated with viscose great smoothness, and at the same time a beautiful lustre, it is advisable to arrange the finishing machine so that the tissue after having been pressed out by the rubber rolls, passes under high pressure through two polished, hollow rolls heated by steam. By this heating, the viscose is instantly con-

verted into insoluble cellulose and the latter is forced into the separate depressions of the tissue, thus imparting to the latter a smooth and lustrous surface.

PREPARATION OF LEATHER–LIKE BODIES BY MEANS OF VISCOSE.

The results of all the attempts to produce a substance with such physical properties, especially as regards tenacity and strength, that it would answer as a substitute for leather, have to be accepted only conditionally, and all products commended under the names of artificial leather or substitutes for leather have to be viewed with a certain mistrust as regards their durability and power of resistance. The reason for the failure to produce a substance which might satisfactorily replace leather, is found in the nature of the latter material itself.

Leather is the portion of the animal skin to which the term *corium* is applied. When a piece of corium is examined under the microscope, it will be seen to consist of innumerable fibres twisted together, forming an extremely tough substance. By the tanning process the fibres of the corium are coated with a tanning substance which prevents the individual fibres, in drying, from adhering firmly together as is the case in raw hide, the latter drying to a hard horny substance, while leather remains flexible.

Hence, if a substance is to be produced which shall to a certain extent possess the characteristic strength, tenacity and durability of leather, it has to be prepared in such a manner that in structure it approaches that of leather. The main point is, therefore, to use a tissue of great strength and tenacity, and to envelop its individual fibres with a substance possessing also great strength and tenacity. With reference to these properties, viscose, or viscoid formed from it, plays, as will be directly shown, an important part, there being no other known body so suitable for the purpose.

Hence, in order to produce a substance which as regards

its properties, is to resemble leather as closely as possible, a tissue of suitable quality has to be throughout saturated with viscose.

Since in this manner masses may be prepared which resemble the finest qualities of glove leather, as well as others which come up to sole leather, great care will have to be bestowed in the commencement of the operation upon the fabric to be manipulated. For very thin masses, which, as regards their properties, are to resemble glove leather, closely-woven cotton fabrics are very suitable, and as the strength of every kind of tissue is considerably impaired by bleaching, it is advisable to use only unbleached tissues except in case the material to be prepared is to be of a pure white color. For the imitation of thicker varieties of leather, such as uppers for shoes, a coarser fabric of strong, unbleached linen may be employed, as well as a tissue of very tough Manila hemp. Finally, for the imitation of the heaviest varieties of leather, thick fabrics of very tough fibres are used. Such fabrics should be prepared by combining the finest fibres by doubling to coarser fibres which, when interwoven, yield a tissue of special strength and tenacity.

In working up these various fabrics into leather-like masses, they are throughout saturated with viscose solution and made uniform by subsequent mechanical treatment, care being taken to keep the structure of the fabric entirely in the back ground, giving the material as far as possible the appearance of leather.

The viscose solutions used for impregnating the tissues should not be too thinly-fluid, a solution containing about 20 per cent. of viscose being probably most suitable. The use of a more highly concentrated solution would not seem to be advisable, because it is then so thickly-fluid as to penetrate only with great difficulty into the interior of the fabric. Entirely satisfactory results are only obtained when the tissue has been saturated throughout its entire thick-

ness, so that on examining with a magnifying glass the cross section of the finished product, the centre presents the same appearance as the portions nearer the surface.

The first step in the operation is the removal of all moisture from the fabric by drying it thoroughly, best by means of hot air. It is then placed in a box, closed air-tight, in which it remains until cooled to the ordinary temperature, and ready for impregnation. The object of this drying is to open the pores of the fabric so that it can be readily penetrated by the viscose solution.

Imitations of leather being, as a rule, colored, dyeing is effected at the same time as impregnation, the appropriate coloring matter being added to the viscose solution, the quantity of coloring matter required for the various kinds of fabrics being determined by experiments. Thick fabrics require less coloring matter than thin ones, because by reason of the fibres in the body of the tissue being also colored, the coloration on the surface appears more vivid than is the case with thin fabrics.

The vat containing the viscose solution should on one side be provided with an opening for the entrance of the fabric winding off a roll. The fabric is carried below the level of the fluid by three rolls revolving with ease. Over the second of these rolls is fixed a pair of rolls so arranged that the distance between the two rolls can at pleasure be decreased or increased. This pair of rolls is set to correspond with the thickness of the fabric so that after the latter has been impregnated with viscose solution, it is only pressed out sufficiently to throw off the excess of fluid adhering to it, which falls back into the vat.

The fabric is passed through the viscose solution with sufficient rapidity to allow of its being saturated throughout its entire thickness. The rate of speed must be slight for thick fabrics, and has to be determined by direct experiments. The fabric coming from the impregnating vat is passed through rolls heated to between 122° and 140° F.,

being slightly squeezed thereby without being actually pressed. Heating to the above-mentioned temperature is best effected by hollow rolls heated by steam constantly passing through them. During the passage of the fabric between these heated rolls, the conversion of viscose into viscoid takes place, one hot pair of rolls being, as a rule, sufficient for thin fabrics, while for thick fabrics a second or third pair of rolls will have to be used.

In place of using heated rolls, the fabric may be simply passed over loosely-lying rolls while a current of hot air ascends from beneath, the viscose being, in this case, also decomposed.

As has been previously explained, by the decomposition of the viscose, vapors of carbon disulphide and other gases are constantly disengaged. To protect the workmen from these injurious vapors, the rolls through and over which the fabrics pass, should be placed in a closed box, and the latter be connected with a ventilator, which constantly sucks air into the box and carries it off. It is advisable to connect the ventilator to a fire-box in which the carbon disulphide vapors are burned to sulphurous and carbonic acids.

When working on a large scale, it will certainly pay to recover and condense the carbon disulphide vapors. For this purpose provision has to be made for a long coil placed in a vessel filled with cold water, in which the warm air and the vapors carried along with it are first cooled to the ordinary temperature. From this preparatory cooler, the vapors are driven into a vessel filled with ice, in which the carbon disulphide vapor is condensed and runs off with the ice water.

The fabrics having been carried through the heated rolls or over a current of hot air, are next exposed to strong pressure by being passed between smooth rolls, in order to give them an entirely smooth surface. They are then repeatedly washed in water to free them from alkali, and are finally dried in the air or in artifically-heated rooms.

In working thick fabrics, one impregnation with viscose solution is frequently found insufficient to saturate them throughout their entire thickness. Such fabrics having been passed through the heated rolls and cooled to the ordinary temperature, are subjected to another treatment with viscose solution, the operation being exactly the same as previously described.

The fabrics impregnated according to the process given above are now in the following condition: All the fibres of the fabric are enveloped by cellulose and the empty spaces between the separate threads and fibres are also filled with it, so that the whole represents quite a uniform mass of cellulose. However, the portion of the mass belonging to the fabric is, in consequence of its structure, exceedingly tough and strong, it having acquired these properties in a still higher degree by being enveloped and cemented by the cellulose. It will be seen that such a fabric, as regards its structure, may be compared with leather, the fibres representing the skin tissue, while the cellulose which envelops them serves for their consolidation and reinforcement.

The impregnated fabrics, when washed and again made air-dry, possess quite a high degree of elasticity and a certain softness, and can without difficulty be further worked by mechanical means. By passing them through brightly polished rolls capable of producing great pressure, they acquire a very smooth surface and high lustre. After going through these rolls they may be passed through others engraved in various ways, for instance, for the imitation of morocco leather. When coloring has been properly done, such imitation can scarcely be distinguished from the genuine product.

However, success in giving a fine appearance to an article to be used, is of only secondary importance, since by coloring and pressing paper it may be given a striking resemblance to morocco leather. But imitations of leather made according to the process given above, have in addition

to appearance another valuable property, namely, strength and tenacity of substance. A piece of leather may be torn with greater ease than a piece of fabric of the same thickness impregnated with cellulose.

Thick fabrics impregnated with cellulose may be used for shoe soles, since they have the advantage over leather soles of not becoming soft when exposed for a long time to dampness and shriveling to a hard mass as is the case with leather which by the action of moisture is deprived of a large portion of its content of tannin. Impregnated fabrics being entirely indifferent towards water are only gradually destroyed by the mechanical wear and tear in using the shoes.

Leather belts for machines are, as is well known, quite expensive, as they have to be made of the heaviest and most carefully tanned qualities of leather. They may, however, be advantageously replaced by belts made of very strong fabrics impregnated with cellulose. Such belts up to 0.39 to 0.59 inch thick are produced by impregnating thinner fabrics and cementing them together with viscose solution.

In the above explanations, the principal elements have been given which must be adhered to in the preparation of imitations of leather in order to obtain satisfactory results, and by observing them it will not be difficult for a manufacturer who takes up the subject, to prepare various products which possess the character of the leather to be imitated, and are distinguished by considerable strength.

However, not only tissues can be converted into leather-like masses, but also fabrics of a felt-like nature, such as felt itself, further felted cotton, and pasteboard.

When ordinary pasteboard prepared from mechanical wood-pulp be throughout saturated with viscose solution and then, under constantly increasing pressure, passed between smooth rolls, a mass is obtained which in hardness considerably surpasses the best quality of pressing-board, and, as regards tenacity and elasticity, can only be com-

pared with very hard wood. It can be worked with all kinds of wood-working tools. On the other hand, it can, while still wet, be pressed into any desired form by suitable dies, and thus plates may be produced which equal in appearance carved wood, and may to advantage be utilized in the manufacture of furniture. By the use of engraved plates which may also be provided with high reliefs, book covers of elegant appearance may be produced from paste-board thus prepared, these book covers having, independent of their cheapness, the advantage of being almost indestructible.

Since paste-board plates only 0.19 inch thick, possess, when impregnated with cellulose, a strength and power of resistance equal to that of quite thick boards, they would seem to be an excellent material for the construction of portable houses, such as are required for scientific expeditions, for the erection of observatories upon high mountains, etc.

Such plates can be rendered fire-proof by treating them, while still moist, with alum solution, and then with water-glass solution, so that a house constructed from this light material can scarcely burn down.

Genuine felt consists of tangled animal hair combined by fulling and beating to a quite solid, and at the same time porous, mass. By reason of its porous nature it can be readily impregnated with fluids. Felt plates impregnated with viscose solution completely retain their flexibility and suppleness, and being waterproof, may be used for hats, clothing, tents, etc. If, previous to their being treated with viscose solution, they are soaked in a saturated solution of borax in water, and then thoroughly dried, they become absolutely indestructible, the rotting of the felt by repeated exposure to moisture being prevented by the highly antiseptic properties characteristic of boric acid. Hence felt-plates prepared in this manner can be laid directly in the ground as a support for heavy machinery, and thus the

noise of the latter, when resting upon an unyielding foundation, can be almost entirely obviated.

VISCOSE IN THE MANUFACTURE OF ARTIFICIAL FLOWERS.

For the manufacture of imitations of flowers, leaves, etc., variously-colored stuffs, as well as paper, are used, the substances being appropriately shaped, then painted, and, if required, varnished. Although, as regards artistic execution, such artificial flowers are beautiful, they delineate only in a very incomplete manner the appearance of natural flowers and leaves.

Great progress was made by the introduction of celluloid in the manufacture of artificial flowers as this material can be readily colored any shade, and moulded into any desired form. The high lustre peculiar to articles of celluloid had, in this case, the effect of still further increasing the beautiful appearance of such artificial flowers. But they are unfortunately quite expensive, and possess the further disadvantage of being extremely inflammable.

However, in viscose the manufacturer has at his disposal a material which deserves consideration, it being not only very cheap, no more inflammable than ordinary paper, and possesses other advantages which make it very suitable for the object in question. The mode of application in the manufacture of artificial flowers would probably be to saturate thin, porous tissue-paper with appropriately-colored viscose, and to cut out the flowers, leaves, etc., by means of heated dies. By contact with the heated die, the viscose is rapidly changed to viscoid, and the leaves, etc., retain exactly the shape given to them by the dies. The leaves are smooth and lustrous and, of course, have all the properties belonging to viscoid. They may be immersed in water without losing their shape or suffering any other injury, and when they have become unsightly by dust, they may even be cleansed by means of an atomizer and water.

For especially delicate artificial flowers, pure viscose may

be used by allowing a thick viscose solution to dry upon glass plates to thin plates and making the leaves, etc., from the latter. By adding sufficient quantities of coloring matter to the viscose solution, colored, transparent leaves of viscoid are obtained which, when worked into flowers, produce a peculiar effect resembling that seen in glass flowers.

VISCOSE IN PHOTOGRAPHY.

Some kinds of photographic apparatus are so arranged that the picture is taken upon a transparent film, instead of upon a glass plate. Such a film can be produced of any length and wound upon a roll, and the use of such a photographic apparatus is very convenient, especially in expeditions, as it requires but little space, and a large number of pictures can be readily taken.

At present the films are almost exclusively made of celluloid membranes, which, however, are not so well adapted for the purpose as viscose, the latter being less inflammable, and less sensitive to moisture and heat than celluloid.

The preparation of films from viscose is a very simple matter. The length of a film being generally such that twelve pictures can be taken with one roll of it, a piece of plate glass corresponding in length to that of the roll of film has to be procured, allowing in addition a few centimeters for the portion of the film secured to the roll. The film being, as a rule, larger in width than in thickness, the plate glass should be wide enough to allow of a large film-plate being at one time made, which is then cut up.

The plate-glass is surrounded by a metal frame projecting a few millimeters above it, its object being to prevent the viscose solution from running off the plate-glass. The latter is placed upon a stand provided with a ball-joint capable of being turned by friction, so that the plate-glass can be readily set in a level position.

The viscose solution used for the preparation of films

should be of such concentration that, when poured in a layer of a fixed depth upon the plate-glass, it yields, after drying, a membrane of sufficient thickness; this can be readily ascertained by a few experiments. The viscose solution is poured upon the plate glass by commencing in one corner of the latter, care being taken that no bubbles are formed, and as the fluid spreads out over the plate-glass, pouring is continued until the entire surface of the plate-glass is uniformly covered.

The plate-glass is then left standing without being touched until the viscose layer is entirely congealed. It is then taken off and heated upon a plate of aluminium sheet to 212° F., until it has become insoluble. It is then washed with water and completely dried in the air. The large plate of viscoid, which should have the appearance of colorless glass, is then cut up into strips of film of suitable length, and the latter are treated with chemicals to form a layer sensitive to light upon their surfaces.

VISCOID MASSES.

If a viscose solution be allowed to stand quietly at the ordinary, or a somewhat higher, temperature, it decomposes slowly, and a plate remains behind, the thickness of which depends on the depth of the original viscose solution. In order to obtain homogeneous viscose masses free from bubbles, the decomposition of the mass should not be hastened by heating, as otherwise the vapors and gases escaping from the mass after it has already become thickly-fluid, would cause the formation of bubbles in it, such as may be observed in ordinary glass. If, on the other hand, the mass is allowed to stand at the ordinary temperature until it has acquired the consistence of solid jelly, it may be carefully lifted from the vessel containing it and placed upon a glass plate, the latter being allowed to lie in a place free from dust until the mass is entirely solid. It is then slowly heated to 212° F., so that it becomes heated throughout,

and then placed in water for the purpose of dissolving the salts present. By exposing such a block to a strong pressure, allowing it to stand under it for some time, a body is obtained which, in appearance, does not much differ from a block of glass.

This pure viscoid may be worked with all kinds of tools. It can be sawed, drilled and worked in the lathe, and forms an excellent material for the manufacture of various fancy articles. If a coloring matter insoluble in water has been added to the viscose solution, the viscoid also appears colored.

Since by mixing viscose with various indifferent bodies, masses may be prepared which present a pleasing appearance, and are much cheaper than pure viscoid by itself, they may be advantageously used for the production of numerous small fancy articles. When properly made they present almost exactly the same appearance as celluloid articles, but are much cheaper and not so inflammable.

Viscose possessing great viscosity, considerable quantities of foreign bodies can be incorporated with it and the resulting viscoid masses be nevertheless very strong, and of beautiful appearance. There are a large number of substances which may be used for filling viscoid masses, and in fact every kind of pulverulent body which is chemically indifferent to viscose may thus be employed. For the preparation of white masses there are, for instance, available, pulverized chalk, plaster of Paris, magnesium carbonate, zinc white, powdered talc (soapstone powder) and pulverized heavy spar, or preferably artificially-prepared heavy spar, the so-called permanent white, which is an extremely delicate powder. According to the substance used, there will be considerable difference in the resulting masses as regards weight, and partially also as regards lustre. Masses of a pure milk-white color and of comparatively slight specific gravity can be produced with the use of magnesium carbonate, the latter being a pure white powder of very slight

specific gravity. Masses prepared with pulverized chalk or plaster of Paris, though light, are heavier than magnesium masses.

The lightest viscoid masses of a white color are prepared by mixing with the viscose as a filling-substance bleached cellulose made from wood by the sulphite or soda process. A product of not quite such a pure white color, but nevertheless of nice appearance, is obtained with the use of mechanical wood-pulp prepared from a white wood, for instance, aspen; such masses have a very slight yellowish tint.

Since viscose solution may be colored as desired, the white basis-masses given above may be used for the preparation of colored viscoid masses, though the latter may also be obtained by mixing with the white pulverulent filling substances other colored powders.

Viscose solutions, even if quite dilute, possess a considerable degree of viscosity, and the preparation of homogeneous masses with the use of filling-substances presents certain difficulties, uniform mixing of the solution with the powders being only accomplished by long-continued manipulation. Besides, the various powders act differently in this respect towards viscose, and it is advisable first to make experiments on a small scale. For this purpose a fixed quantity of dilute (at the utmost 10 per cent.) viscose solution and a fixed quantity of the powder to be used for filling are employed, for instance, 1 quart of viscose and 22 lbs. of powder. Pour the viscose into a large, round vessel, smooth inside, for instance, a porcelain dish, and while one workman constantly stirs the viscose, another one pours the powder in a fine jet into the fluid until a thick paste is formed, which cannot be further worked with the stirrer.

This paste is rolled out on a smooth plate—a marble slab being very suitable for the purpose—and the plate thus obtained is folded over and again rolled out, the operation being repeated until a uniform mass is obtained which is

still sufficiently plastic that, when subjected to quite a strong pressure in a mould, all the elevations and depressions are reproduced. The moulded articles are allowed to stand quietly until perfectly dry. The quality of these test-pieces furnishes accurate information regarding the properties of the mass.

A viscoid mass of the proper quality should possess beautiful lustre, and be so hard and solid that it can only be broken with difficulty by vigorous blows with a hammer. When the mass breaks under the hammer into several pieces, and consequently is brittle, it is indicative of too large a quantity of filling-substance having been used. In this case the fractures are very uneven, dull and lustreless, while, on the other hand, the fracture of a mass containing not too large a quantity of filling-substance should be conchoidal, with sharp, smooth edges, and lustrous.

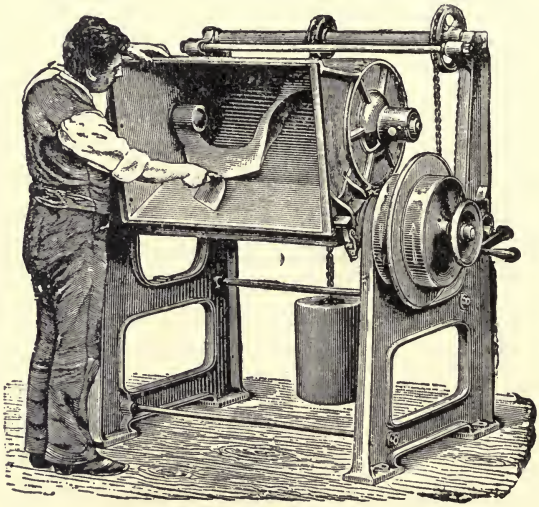
When the quality of the test-mass is found to come up to the standard, the composition of the mass for the preparation of larger quantities of it can be calculated from the amount of filling-substance and viscose solution used.

For the preparation of larger quantities of viscoid masses special mechanical contrivances have to be employed which allow of the thorough kneading together of the fluid and the powder. Mixing or kneading machines, such, for instance, as imitate kneading bread-dough by hand, are best adapted for the purpose, since with such machines any desired power may be applied. Mixing and kneading machines of this kind performing excellent work are, for instance, constructed by Werner and Pfleiderer, the work of thorough mixing being effected by an implement of peculiar construction, the so-called mixing paddle. A large number of machines of this kind are at present in use in bread bakeries, paint factories—in fact in all kinds of establishments where masses have to be mixed and kneaded—and are most suitable for the preparation of viscoid masses. However, to adapt them entirely for this purpose, the mix-

ing vessel must be so arranged that it can be tightly closed, so that the viscose does not decompose during the operation, since decomposition should only be effected when the plastic mass is brought into the form the finished article is to have. Fig. 32 shows the peculiar shape of a kneading and mixing paddle of a kneading and mixing machine constructed by Werner and Pfleiderer.

In the commencement of the operation, the entire quantity of viscose solution to be worked is brought into the

Fig. 32.



mixing vessel, and through a funnel placed in the lid of the mixing vessel the powder is allowed to run in in a thin jet, while the mixing paddle revolves with moderate velocity. When, in consequence of the increasing viscosity of the mass, its resistance to the mixing paddle becomes greater, the velocity of the latter is increased, and thus continued until a sample taken from the mixing vessel shows the mass to be entirely uniform. The machine is then stopped, the viscoid mass taken out and immediately moulded.

The moulds used may be made of iron or brass, or of wood, gutta-percha, or of plaster of Paris impregnated with stearin. Moulds which are most frequently used should, of course, be made of metal, this material possessing the greatest power of resistance and being less subject to wear and tear.

It depends on the article to be prepared whether it is to be moulded solid or hollow. Billiard balls, door-handles, buttons, ornaments in relief, etc., are moulded solid. For the preparation of balls, hemispherical moulds are used. They are pressed full of viscoid mass and, after coating two such hemispheres with a small quantity of thick viscose solution, they are joined together by vigorous pressure. In this manner cane-heads, door-knobs, etc., are made.

For moulding hollow articles, plates of the thickness the articles are to have are first prepared from the mass. Such a plate is pressed into the hollow mould, the core portion of the mould is then laid upon it, and the mould thus put together is subjected to pressure in a press, by which any excess of mass is forced from the mould. When the press is opened the core portion of the mould is first lifted off, and the article can then be readily detached by turning the mould over and giving it a gentle knock. Doll-heads are thus made in two halves, which are then cemented together with viscose solution.

The articles when taken from the moulds being still soft have to be carefully laid upon a smooth board and allowed to remain in a place free from dust until they are solid, hard and dry. They are then finished by heating to about 212° F. In case the articles should turn out lustreless, a beautiful lustre can be given to them by applying a coat of dilute (10 per cent.) viscose solution. When the articles are to be painted, for instance, doll-heads, the colors are applied to the finished article, a coating of viscose solution being finally put on. The colors then lie under a thin colorless layer of cellulose similar to a coat of a protecting

glaze, and the articles may be cleansed with soap and water without injury to the colors.

Viscoid masses, the filling-substances of which consist of cellulose or mechanical wood-pulp, acquire a hardness not surpassed by hard wood, and may be advantageously used for machine parts which otherwise have to be made by hand from wood. Screws and nuts may thus, for instance, be made from the mass while still soft, and they do not require finishing by hand, because coming from the same mould they have the same gauge. In the same manner shuttles, spools, small cog-wheels, etc., may be prepared by pressing, the cost of producing such articles being, as may readily be conceived, very slight as compared with those made by hand from wood.

Viscoid masses filled either with cellulose, mechanical wood-pulp, or indifferent mineral powders possess in a high degree the power of resisting atmospheric influences, and suffer neither from rain or frost. In consequence of these valuable properties they are well adapted for building purposes, for the exterior as well as the interior of houses. Mouldings, cornices, lion heads and other constructive ornaments may be advantageously made of this mass, which is cheap, and at the same time capable of great resistance, and it may also be used for busts, statuettes and ceramic articles.

VIII.

NITRO-CELLULOSE (GUN-COTTON, PYROXYLIN).

When pure cellulose is brought in contact with more or less concentrated nitric acid, a large number of combinations is formed, the kind of combinations which are formed depending on the concentration of the acid, as well as on the time it remains in contact with the cellulose. However, there are two distinctly marked groups of combinations, one of them being distinguished by its members exploding with great violence when brought in contact with a red-hot body, as well as by concussion and percussion, and further by being indifferent towards solvents. The second group, to be sure, also contains explosive bodies, they being, however, distinguished by the property of completely dissolving in certain fluids. Hence we may speak of explosive nitro-celluloses and soluble ones, but it must be expressly understood that an absolutely sharp boundary between these two groups is not known.

The combinations formed by the action of nitric acid upon cellulose were simultaneously discovered by Braconnet, Schönbein, Otto and Pelouze, the explosive products for blasting and military purposes being first prepared by them. The properties of the less explosive, but readily soluble, combinations, as well as the numerous uses to which they could be applied, became accurately known only at a much later time. They are at present so numerous that several large industries—manufacture of artificial silk and of celluloid—are based upon them.

According to former opinions regarding the formation and composition of the combinations belonging to these

groups, they were considered as nitro-compounds. In accordance with this assumption, by treating cellulose with nitric acid, the water is withdrawn from the cellulose and replaced by nitryl, the radical of nitric acid. However, when it was found that by treating cellulose for a longer or shorter time, as well as at different temperatures, with varying quantities of nitric acid, combinations containing different quantities of nitrogen were formed, it was sought to explain this phenomenon by the existence of different kinds of nitro-cellulose, and thus hypothetical compounds which were to contain 1 to 11 molecules of nitryl were arrived at. It was further considered justifiable to assume that nitro-celluloses with a certain content of nitrogen are insoluble, while others constitute the soluble form. However, since nitro-celluloses can be prepared which possess nearly the same content of nitrogen, but one of which is insoluble and the other readily soluble, these opinions can no longer be considered correct.

According to modern views regarding the composition of gun-cotton, it cannot be designated a nitro-compound, but has to be termed a nitric acid ester or ether, the proof of the correctness of this view being found in the behavior of gun-cotton towards different reagents. In treating gun-cotton with concentrated sulphuric acid it is slowly decomposed, even at the ordinary temperature, and nitric acid is liberated. If gun-cotton be treated with potash-lye it is, even if only slightly heated, completely decomposed, potassium nitrate being formed, and the cellulose with all its properties reappears. Even ferrous chloride acts upon nitro-cellulose in such a way, that the formation of ferric chloride is caused by the nitric acid which is liberated, and cellulose is again formed.

In view of these reactions the assumption that the so-called nitro-cellulose is a combination formed by the replacement of the hydrogen in the cellulose by the radical nitryl can no longer be maintained, and the view that a

series of combinations of cellulose with nitric acid—cellulose nitric acid esters—is in question, would seem to be correct. From this also results the assumption of a mono-cellulose, di-cellulose, tri-cellulose, up to endeca-cellulose, and the quantity of nitrogen found in the products depends on the concentration of the nitric acid used, as well as on the duration of the action of the acid upon the cellulose.

Nitro-cellulose, in explosive as well as soluble form, may be prepared by bringing pure cellulose in contact with highly concentrated nitric acid, but as the latter by the absorption of water becomes in a short time less concentrated, mixtures of nitric and sulphuric acids are generally used as nitrating fluids. Sulphuric acid being a body which fixes water with great energy, its purpose in this case, is to absorb the water which is formed, so that the concentration of the nitric acid remains the same.

This assumption, however, does not agree with the facts which have been established in reference to the behavior of cellulose towards mixtures of very varying quantities of nitric and sulphuric acids. From investigations of the products thus formed it would appear that the kind of combination formed is very materially influenced by the larger or smaller quantity of sulphuric acid present.

For an explanation of these facts we are indebted to the thorough investigations made conjointly by G. Lunge and E. Weintraub, and the points of practical importance for the preparation of nitro-cellulose will here be briefly given.

The larger the quantity of sulphuric acid in the nitrating fluid in comparison with that of nitric acid, the more slowly the entire process is completed. By using $\frac{1}{4}$ part of sulphuric acid to 1 part of nitric acid, reaction is complete in half an hour. (It may be here remarked that the course of the reaction may be measured by the quantity of nitrogen present in the newly-formed nitro-product.) With the use of a mixture of 3 parts of sulphuric acid and 1 part of nitric acid the content of nitrogen in the product is in the

course of half an hour much lower than with the use of the previous mixture. If, finally, a fluid of 8 parts sulphuric acid and 1 part nitric acid be employed, reaction is not complete even in a month.

With a slower course of reaction the content of nitrogen in the product is also changed, *i. e.*, with an increasing content of sulphuric acid in the nitrating fluid, final products are obtained which contain less nitrogen than with the use of a smaller quantity of sulphuric acid.

The presence of a very large quantity of sulphuric acid (more than 8 to 1) in the nitrating fluid appears to be the reason why, even after remaining for so long a time in contact with the fluid, a certain quantity of the cellulose itself remains unchanged and is not converted into a nitro-compound. In our opinion, an explanation of this phenomenon may be found in the fact that, in the commencement of the operation, certain fibres of the cellulose are already changed by the sulphuric acid in a manner similar to that when cellulose is converted into vegetable parchment, and thus become inaccessible to the action of the nitric acid. That the presence of a larger quantity of sulphuric acid in the nitrating fluid exerts a material influence upon the physical structure of the product has been confirmed by the investigations above referred to.

With the use of a nitrating fluid containing but a small quantity of sulphuric acid—about $\frac{1}{4}$ to $\frac{1}{2}$ of the weight of nitric acid—a product is obtained which possesses greater strength than the cellulose originally used, the fibres appearing strongly contracted. If, on the other hand, fluids rich in sulphuric acid (7 to 1 upwards) are employed, the dry product represents a finely-fibered powder.

The process of nitration is completed the more rapidly the higher the temperature of the fluids is, it being effected in the shortest time at between 140° and 176° F. In practice it is, however, not feasible to work with such a high temperature, the yield of nitro-cellulose becoming con-

stantly smaller with an increasing temperature, and a considerable portion of the substance passing into solution.

When working with a nitrating fluid heated to 140° F., nitration may be considered complete in half an hour. The loss in cellulose was found, in this case, to amount to 1.95 per cent. By leaving the finished product in the hot fluid, 5.67 per cent. of it was in the course of 4½ hours again destroyed.

With the use of a fluid heated to 176° F., the destructive processes became still more conspicuous, and nitration, in this case, was generally complete in less than a quarter of an hour. The loss in cellulose amounted to 6.25 per cent., increasing in half an hour to 27.45 per cent., and in three hours to 52.76 per cent.

By nitration at higher temperatures, a change in the structure of the nitro-cellulose takes place, it becoming short-fibered and brittle, and the product prepared under these conditions appears, after drying, as a finely-fibered powder.

Towards polarized light, nitro-cellulose acts in a very peculiar manner, it having been asserted by some investigators that the different degrees of nitration may be recognized from the appearance of the fibres when observed in polarized light. However, Lunge and Weintraub specify this as not being pertinent.

In polarized light the highest degrees of nitration appear pale to dark blue. However, important information regarding the presence of unchanged cellulose is gained by examining nitro-cellulose in polarized light, the unchanged cellulose appearing pale yellow to reddish, and lights up more than nitro-cellulose. It is, however, impossible to determine from the picture in the polarizing microscope the quantity of non-nitrated cellulose. If the latter amounts to only 5 per cent., a large portion of the field of vision appears already of a yellow color, and, if the content of cellulose increases to 10 or 15 per cent., it is no longer

possible to observe the polarizing phenomena of the nitro-cellulose, they being completely hid by those of the cellulose.

Although the disclosures afforded by observing the fibres under the polarizing microscope are quite uncertain, they may nevertheless be utilized for gaining information in regard to the state of nitration as, for instance, is done by Chardonnet, in testing the nitro-cellulose which is to be used for the preparation of artificial silk (see later on). When the field of view shows exclusively blue-appearing fibres, and no yellow ones can be seen, it is, at all events, a proof that the total quantity of cellulose used has been nitrated, and that the product is very likely completely soluble.

In practice two main objects are especially to be attained in the preparation of nitro-cellulose, namely, the product must either be explosive to the highest degree, *i. e.*, gun-cotton in the actual sense of the word, or it must dissolve in solvents without leaving a residue, the term *collodion cotton* being, in the latter case, generally applied to the product.

In conducting the nitration of cellulose it is scarcely probable that a product is obtained which is in accordance with a positively determined combination, *i. e.*, a nitro-cellulose of positively determined composition, the result being, on the contrary, always mixtures of various degrees of nitration with more or less changed cellulose.

For practical purposes two products of different properties come chiefly into question, namely, on the one hand, the preparation of a nitro-cellulose which, in exploding, produces the greatest dynamic effect and is suitable for the manufacture of blasting gelatine, and on the other, the production of a nitro-cellulose which can be completely dissolved. The latter product has attained great importance for photographic use, and the manufacture of artificial silk.

Information regarding the composition of nitro-cellulose produced by a certain process is sought to be obtained by

establishing the quantities of nitrogen contained in them. While the French chemists calculate the nitrogen in the form of nitric oxide which can be obtained from 1 gramme substance (reduced to 0° and 760 millimeters height of barometer), the English and German chemists give the content of nitrogen directly in per cent.

Conjointly with J. Bebie, G. Lunge has recently occupied himself with the composition and properties of the various nitro-celluloses, and in the commencement of a very full article published in the "Zeitschrift für angewandte Chemie," 1901, these investigators give the relation between the modes of determination adopted by the French and German chemists, as shown in the table below, which affords a ready comparison between the two methods of examination.

Name.		Formula.	Ccm. nitric oxide (NO) in 1 g.	Per cent. nitrogen (N) in 1 g.
Dodeca-	nitro-cellulose.	$C_{24}H_{28}O_8(NO_3)_{12}$	226.17	14.14
Endeca-		$C_{24}H_{29}O_9(NO_3)_{11}$	215.17	13.47
Deca-		$C_{24}H_{30}O_{10}(NO_3)_{10}$	203.35	12.75
Ennea-		$C_{24}H_{31}O_{11}(NO_3)_9$	190.75	11.96
Octo-		$C_{24}H_{32}O_{12}(NO_3)_8$	177.19	11.11
Hepta-		$C_{24}H_{33}O_{13}(NO_3)_7$	162.36	10.18
Hexa-		$C_{24}H_{34}O_{14}(NO_3)_6$	145.93	9.15
Penta-		$C_{24}H_{35}O_{15}(NO_3)_5$	127.91	8.62
Tetra-		$C_{24}H_{36}O_{16}(NO_3)_4$	107.81	6.76

According to the investigations of the above-mentioned scientists, the degrees of nitration from tetra-nitro-cellulose to deca-nitro-cellulose can only be obtained by treating cotton with nitric acid, while for still higher degrees of nitration, mixtures of nitric and sulphuric acids have to be employed. Since in the preparation of nitro-cellulose on a large scale, mixtures of nitric and sulphuric acids are always used, such mixtures were almost exclusively employed in the above investigations.

The influence exerted by the content of water in the acid mixture upon the process of nitration is shown by the table below :

Ccm. NO in 1 g.	Per cent. N in 1 g.	Solubility in ether-alcohol (3 : 1).	Yield.	Nitrating mixtures. %		
				Sulphuric acid SO_4H_2.	Nitric acid HNO_3.	Water H_2O.
217.73	13.65	1.50	177.5	45.31	49.07	5.62
210.68	13.21	5.40	176.2	42.61	46.01	11.38
203.49	12.76	22.00	—	41.03	44.45	14.52
200.58	12.58	60.00	167.0	40.68	43.85	15.49
196.35	12.31	99.14	159.0	40.14	43.25	16.61
192.15	12.05	99.84	153.0	39.45	42.73	17.82
184.78	11.59	100.02	156.5	38.95	42.15	18.90
174.29	10.93	99.82	144.2	38.43	41:31	20.26
155.73	9.76	74.22	146.0	37.20	40.30	22.50
148.51	9.31	1.15	138.9	36.72	39.78	23.50
133.94	8.40	0.61	131.2	35.87	38.83	25.30
103.69	6.50	1.73	—	34.41	31.17	28.42

The considerable differences appearing in the degrees of nitration between the soluble and insoluble parts might be explained by the dilution of the nitrating mixtures which occurs in the course of reaction, this dilution being due to the withdrawal of nitric acid and to the water formed by the process itself. It having, however, been established by the investigations that a difference of a few per cent. of water suffices to produce degrees of nitration which differ considerably one from the other, it follows that a uniform product is never obtained, but always a mixture of different degrees of nitration. To prevent this as much as possible in practice, the operation should be so conducted that the quantity of nitrating fluid is very large in proportion to cotton, the effect of dilution being then less pronounced.

If the nitrating mixture contains 16.6 per cent. of water a completely soluble product belonging to the group of actual collodion cottons is obtained. From 18 per cent.

up, the content of nitrogen decreases very rapidly with the increase in the content of water.

The entire group of soluble nitro-celluloses between 170 and 196 cubic cm. is defined by a content of water which only amounts to 4 per cent. (16.5 to 20.5 per cent.). Between 7 and 8 lies *the octo-nitro-cellulose with a content of 177.2 cubic cm. of nitrogen which may be designated as the typical soluble nitro-cellulose—the actual collodion cotton. This product is always obtained by working with a nitrating mixture which contains 19.42 per cent. of water.*

This statement is of great importance for the practice, it pointing out the way in which the material required for the production of collodion for photographic purposes, as well as for the manufacture of artificial silk, can be prepared. According to statements made in this direction regarding the manufacture of artificial silk according to Chardonnet, a nitrating fluid composed of 85 parts of sulphuric acid and 15 parts of fuming nitric acid, is for 4 to 6 hours allowed to act upon cotton. However, several chemists in working according to this direction obtained no adequate results, and even with the use of a higher temperature, the results were not more favorable, as shown in the following table :

Temperature.	Duration of nitration.	Ccm. NO in 1 gramme.	Solubility.	Yield.
86° F.	4 hours.	199.89	17.14	160.2
104° F.	7 hours.	209.90	15.54	143.1

The solubility of the products which were last obtained is only slight, nitration, however, being complete, and in polarized light all the fibres appear of a slightly steel-blue color. However, it may in this case be remarked that with nitro-cellulose with a content of nitrogen below 190 cubic cm., blue lighting up could never be observed.

The solubility of nitro-celluloses with a content below

160 cubic cm. decreases, the degrees of nitration from hexa-nitro-cellulose downward being insoluble in ether-alcohol. According to Eders' investigations, which chiefly referred to the preparation of collodion-cottons, di-nitro-cellulose and tri-nitro-cellulose are soluble combinations. (See soluble gun-cotton or collodion-cotton later on).

With a still greater increase in the content of water, the nitrating effect decreases very much, and the entire process seems to be turned in another direction, products possessing the properties of oxy-cellulose being now formed. They are soluble in dilute alkalies and can be again separated from these solutions by acids or alcohol. When brought in contact with basic coloring matters, they acquire an intense coloration, reduce Fehling's solution, and yield combinations of phenyl-hydrazine.

The effect of higher temperatures such as are used in the preparation of collodion cottons is shown by the summary, given below, of a few experiments made in this respect with the use of a nitrating fluid which contained 18.9 per cent. of water.

Duration of nitration.	Temperature Degrees F.	Ccm. NO in 1 g.	Solubility in ether-alcohol.	Yield.
4 hours.	62.6	183.54	95.60	155.1
24 hours.	62.6	184.78	99.81	156.2
4 hours.	104	183.40	99.58	148.1
4 hours.	140	172.48	99.82	52.0
¼ hour.	140	182.80	99.71	146.7

As shown by these figures, nitration was complete in 4 hours at the ordinary temperature and the yield was greater than at 104° F., but the product dissolved with greater difficulty and less completely in the mixture of ether and alcohol. By increasing the temperature to 140° F., partial denitration took place rapidly. After 4 hours the content of nitrogen had dropped to 172.48 cubic cm. By allowing

the acid to act, at such a high temperature, only for a short time, for instance, ¼ hour, nitration is complete, but if this time be exceeded, a decrease in the content of nitrogen immediately takes place.

Simultaneously with denitration, the structure of the cotton is also completely destroyed; it crumbles to a delicate paste, a pulverulent mass remaining behind after drying. The structure of the nitrated cotton is also affected by the content of water in the nitrating fluid. Up to a content of water of 15 per cent., scarcely any change in the structure is observed, but from 18 per cent. up, the fibres are somewhat contracted and the peculiar twist characteristic of cotton disappears. With a still larger content of water the structure of the fibres is almost completely destroyed; the cavity is torn open, and the fibres crumble to small fragments which felt together in knotty masses. The destructive effect is greatest when the content of water reaches 23 to 25 per cent.

Although all the nitro-celluloses up to the deca-combination can be produced with the use of nitric acid alone, a mixture of nitric and sulphuric acids is generally used for the preparation of collodion cotton, a saving of nitric acid being thereby effected and the time of reaction shortened. With the use of a mixture of 1 nitric acid to 3 sulphuric acid the following figures were obtained:

Experiment.	Ccm. NO. in 1 g.	Per cent. N.	Solubility in ether-alcohol.	Yield.	Proportion of cellulose to nitric acid.
1	210.69	13.21	3.20	174	
2	198.10	12.42	98.70	160	1 : 30
3	186.00	11.72	99.28	157	
4	174.81	10.96	99.50	148	
5	187.30	11.74	99.98	159	1 : 12
6	173.83	10.90	99.20	149	

The nitrating fluids used in these experiments were composed as follows:

Experiment.	1	2	3	4	5	6
H_2SO_4	62.18	61.53	60.30	38.88	59.77	58.34
HNO_3	21.91	20 02	19.71	19.60	20.94	20.62
H_2O	15.91	18.45	19.99	21.52	19.29	21.04

The product obtained by experiment No. 2 closely resembles, as regards its content of nitrogen, as well as its solubility, the preparation to which the term *pyro-collodion* has been applied by Mendelejeff.

The final results of further experiments made with the use of nitric and sulphuric acids in the proportions of 1 : 4 and 1 : 5 are given in the table below:

Experiment.	Ccm. NO in 1 g.	Per cent. N.	Yield.	Proportion of HNO_3 to H_2SO_4.	Proportion of cellulose to HNO_3.
1	192.65	12.08	163		
2	179.10	11.23	153	1 : 3.8	1 : 30
3	187.58	11.76	156		
4	175.23	10.99	151		1 : 12
5	198.32	12.42	167		
6	185.89	11.66	158		1 : 30
7	168.00	10.53	140	1 : 5	1 : 8
8	149.12	9.35	—		

The composition of the nitrating fluids used in these experiments was as follows:

Experiment.	1 and 3	2 and 4	5	6	7	8
H_2SO_4	63.84	62.52	67.60	66.37	64.85	64.11
HNO_3	16.96	16.46	13.66	13.04	14.90	13.62
H_2O	18.20	21.02	18.74	20.59	20.25	22.27

The temperature used in all the experiments was the ordinary one of a room, and the duration of nitration 24 hours.

With the use of nitrating fluids, the acid proportions of which were 1 : 3, 1 : 3.8, and 1 : 5, a few experiments were made at a higher temperature, and at 95° F., after allowing the acid mixture to act for only two hours, the same products as under the above-mentioned conditions were obtained.

When carrying on nitration according to a determined rule, attention has to be chiefly directed to the content of water in the nitrating fluid, the quality of the products obtained being less affected by the larger or smaller quantity of sulphuric acid. A special series of experiments, in which the proportion between nitric acid and water was strictly maintained, while the quantity of sulphuric acid was changed, showed that the products obtained with dilute mixtures have to be considered as nitro-oxycelluloses, or as mixtures of nitro-celluloses with nitro-oxycelluloses. Further experiments showed :

Ccm.NO in 1 g.	Per cent. N.	Yield.	Nitrating fluid.		
			H_2SO_4.	HNO_3.	H_2O.
217.26	13.62	173	60.00	27.43	12.57
219.28	13.75	174	62.10	25.79	12.11
220.66	13.83	175	62.95	24.95	12.10
219.34	13.75	175	63.72	25.31	10.97
218.73	13.71	175	64.56	24.65	10.79

Thus, products were obtained which, as regards their content of nitrogen (up to 13.83 per cent.), more closely approach hexa-nitro-cellulose (14.14 per cent.) than all previous ones produced with nitric and sulphuric acids. The feature of this experiment of value in practice is the fact, that nitro-celluloses with a high content of nitrogen

may be obtained with acid mixtures quite rich in water. By a series of special experiments it was shown that a content within very wide limits of hyponitric acid in the nitric acid exerts no influence whatever upon the course of the process.

The valuable investigations of G. Lunge and J. Bebie conclude with giving analyses of various nitro-celluloses. Samples of collodion cotton were first examined. One of them marked A, came from a Belgian factory, and is used for the preparation of blasting gelatine, while the other, marked B, from a factory at Breitenbach near Zürich, is manufactured for the purpose of preparing artificial silk.

Sample A showed in 1 g. 196.7 Cc.NO = 12.33 per cent. N, a solubility in ether-alcohol of 95.49 per cent., and an exploding point of 389.3° F., after heating during 4′ 46″.

Sample B showed an exploding point of 386.6° F. after heating during 4′ 46″. The most highly nitrated actual gun-cotton from the Eidgenoessischen Munitionsfabrik at Thun proved, in regard to its explosibility, almost identical with the less highly nitrated collodion cotton. In other samples, collodion cotton also showed a somewhat higher exploding point than well-washed gun-cotton, while preparations not thoroughly washed exploded at much lower degrees of heat.

PREPARATION OF GUN-COTTON.

The first requisite for the production of gun-cotton which will in every respect come up to the demands made on it, is the presence of entirely pure cellulose, either purified cotton being used, or more rarely a fine quality of paper containing only cellulose. However, the cost of production being, in the latter case, much higher than with cotton, the latter is always used for manufacturing on a large scale.

Raw cotton contains always certain quantities of fat, wax-like substances, and coloring matter. To free it from these bodies, it is first boiled with weak soda lye in large wooden

vats with the use of steam, then freed from lye by means of a centrifugal, and finally washed with water until all alkaline reaction has disappeared. It is then bleached with chlorine, washed in acidulated water, then in pure water, and is finally freed from water in a centrifugal, and dried. The dry cotton is stored, carefully protected from dust, till it is to be treated with nitric acid. Loose, as well as spun, cotton may be subjected to nitration, but many manufacturers prefer to use loosely-spun cotton, the hanks being more readily handled than the loose, bulky material.

ACID USED FOR NITRATION.

The conversion of cellulose into gun-cotton may be effected by treating it with concentrated nitric acid alone. However, this process is not expedient, since by the absorption of water the nitric acid soon becomes diluted to such an extent that it has to be replaced by fresh acid. At present mixtures of concentrated nitric and sulphuric acids are generally used, the latter acid acting as a water-attracting body, and the concentration of the nitric acid is thus for a longer time maintained at the required degree. Nitration was formerly also effected by introducing thoroughly-dried and finely-pulverized saltpetre into concentrated sulphuric acid, a highly concentrated nitric acid being thus obtained. However, many obstacles being met in completely removing the potassium sulphate, which dissolves with some difficulty, from the gun-cotton by washing, this process has been entirely abandoned, and at present mixtures of the two acids are only used.

For the manufacture of very explosive products, nitric acid as concentrated as possible (specific gravity 1.500) should be used, but for readily soluble products, nitric acid of specific gravity 1.400, and containing in round numbers 65 per cent. of nitric mono-hydrate, suffices. The nitric acid must be entirely free from foreign bodies, and contain but a small quantity of hyponitric acid, the product standing next to it.

The sulphuric acid to be used is the highly concentrated white acid of commerce. It should be free from iron, and contain but a very small quantity (not more than 0.1 per cent.) of arsenic.

Because of their properties, the storage of the acids is connected with some difficulties. The nitric acid should be kept in the carboys in which it is shipped from the factory until it is to be mixed with the sulphuric acid. The store-room in which the carboys are kept should be fireproof, so that in case one of them bursts, and the straw in the basket used for packing ignites, the flames cannot spread. The carboys should be placed so that a bursted carboy can be drawn by means of a hook into the centre of the store-room, and the floor of the latter so planned that the acid can run off into a pit. Only after the burning basket has been entirely consumed, and the room has been thoroughly aired, can the latter be again entered. Pure aluminium being indifferent towards concentrated nitric acid, boiler-like, closed vessels of this material might be used for storing it.

Sulphuric acid of fixed concentration (not below 1.600 specific gravity), as otherwise hydrogen-gas would be evolved, may be kept in iron vessels, old steam boilers being frequently used for this purpose. Iron being brought into a passive state by concentrated nitric acid, nitration may be effected in cast-iron vessels furnished with a contrivance by means of which a large portion of the absorbed fluid may be withdrawn when the cotton has been sufficiently treated.

When working on a very large scale, stoneware vessels standing in a large trough filled with water to prevent strong heating, are preferably used. For introducing and lifting out the cotton a strong glass-rod bent into a hook on one end is employed.

The nitrating fluid is the mixture of nitric and sulphuric acids, in which the cotton to be nitrated is immersed. It

depends on the proportions in which the two acids are mixed, whether a very explosive, but only slightly soluble, mass—gun-cotton in the actual sense of the word—is obtained, or a product only slightly explosive, but readily soluble, to which the term *collodion-cotton* may be applied. The proportions for both these products, as determined by numerous experiments in practice, are as follows:

For explosive gun-cotton: 1 part nitric acid and 3 parts sulphuric acid.

For soluble gun-cotton: Equal parts of nitric acid with 75 per cent. of nitric anhydride and concentrated sulphuric acid with 96 per cent. sulphuric anhydride.

CONDITION OF THE NITRATING FLUID.

The constancy of the composition of the acid mixture is of great importance for the production of a uniform product, whether explosive or soluble. However, in reality, it is quite a difficult matter to maintain this state of the acid mixture, because during nitration water is always formed, causing a dilution of the acid. Theoretically, a certain quantity of acid could be used at one time, but as this is impossible in practice, an effort has to be made to maintain as long as possible the concentration of the acid within certain limits. It would, therefore, seem advisable to use nitrating vessels of comparatively large size, the advantage gained thereby being that the concentration of the acids is not to any considerable extent reduced by successive nitrations. By successive immersions of fresh quantities of cotton in the nitrating vessel, the level of the fluid will fall, but if it be restored to its original height, by a workman allowing fresh acid mixture kept in readiness to run in, the dilution of the acid in the nitrating vessel is decreased by this addition of concentrated acids.

In this manner the operation may for a long time be continued without the necessity of removing the acid mixture on account of its containing too much water. How-

ever, as a rule, the acid has to be earlier removed for another reason. Many fine fibres of gun-cotton collect gradually in the fluid in the nitrating vessel, and when immersing fresh cotton, adhere so firmly to the latter as to greatly retard the penetration of the nitrating fluid. This may to some extent be remedied by taking the acid from the nitrating vessel and filtering it through glass-wool in a stoneware filter, or by bringing it into a tall reservoir and allowing it to stand quietly until the delicate fibres have deposited on the bottom and the supernatant acid is clear.

The nitrating fluids, which have been removed from the nitrating vessels, are always regenerated to be again utilized. In doing this it is absolutely necessary to determine by accurate analysis the quantities of nitric and sulphuric acids, as well as of water, contained in the fluids. Based upon this analysis, it can then be calculated how much of the most highly concentrated acids has to be added to restore the proportion between the acids as required for nitration.

Since by constant regeneration an excessive quantity of exhausted acid would in time be obtained, fuming sulphuric acid is frequently used in place of ordinary sulphuric acid, and when sulphur trioxide can be obtained in commerce at suitable prices, its use for the regeneration of the acid mixture may be recommended. As regards the nitric acid to be employed, it need scarcely be mentioned that it should be as highly concentrated as possible.

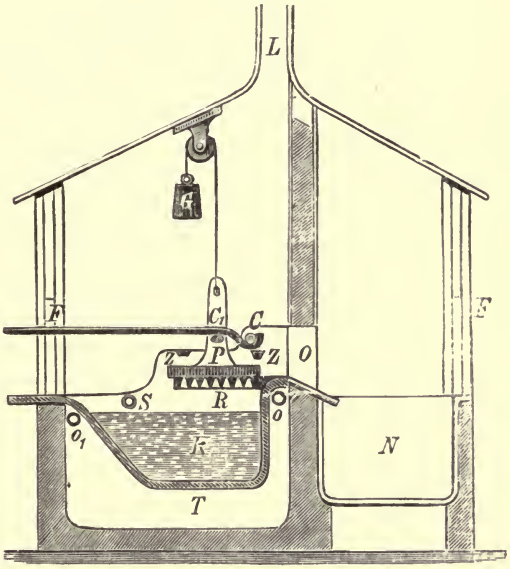
EXECUTION OF NITRATION.

Nitration of the cotton may, as previously mentioned, be effected in stoneware vessels as well as in a cast-iron apparatus. In any case the vessels must be placed in a room provided with contrivances for carrying off the gases evolved during nitration, they having a deleterious effect upon the respiratory organs of the workmen. Hence a ventilating hood connecting above with a pipe is placed over each

nitrating vessel. These pipes terminate in a joint pipe, into which air is constantly sucked by a ventilating contrivance. In smaller plants this air is forced through a layer of red-hot coal, the products of decomposition of the nitric acid being thus rendered innocuous for the neighborhood. In larger factories it is more economical to conduct the air loaded with products of decomposition of the nitric acid into a condensing tower and utilize it again for nitric acid.

Fig. 33 represents an iron nitrating apparatus so arranged

FIG. 33.



that the gun-cotton nitrated in it can at the same time be quite vigorously pressed out. The cast-iron trough *K*, obliquely cut off on the side turned towards the workmen, is surrounded by a vessel *T*, through which water runs constantly, passing in at *O* and passing out at O_1. The object of this arrangement is to carry on the operation always at the same temperature, and therefore hot or cold water is, according to the season of the year, conducted through *T*.

The contrivance for pressing out the nitrated cotton consists of a grate-like iron plate *R*, upon which can be placed a solid iron plate *P*, which is provided with a vertical part C_1 serving as the fulcrum of a lever. When the cotton just lifted out from the acid mixture is spread out upon the grate-like plate by placing the solid plate upon it, it can be vigorously pressed by means of the lever, the acid pressed out running back into the vessel *K*.

The plate *P* is connected with the vertical part *C*. To the latter is secured a chain which runs over a pulley and carries on the upper part the weight *G*. By this weight the plate *P* is raised to the pivot *z z*, so that the cotton lifted out from the nitrating vessel can be placed upon the grate-like plate *R*, and pressed by placing in position the lever which revolves around C_1 the cotton being thus compressed and the fluid pressed out falls back into *K*. The compressed cotton is pushed through the opening *O* and falls into the vessel *N*, where it remains until a sufficiently large quantity for further manipulation has accumulated. The pipe *S* serves for the introduction of fresh quantities of acid, the latter being allowed to run in whenever the level of the fluid falls below a mark on the wall of the vessel *K*.

For the complete protection of the workmen from the vapors evolved by the nitrating fluid, the entire apparatus is enclosed in a case of glass and iron, the two sliding windows *F* and *F* being opened only when cotton is to be introduced, or taken out. The gases escape through the pipe *L*, passing into a chimney in which a gas flame is constantly burning so that the escaping products of decomposition of the nitric acid are completely burnt and cannot inconvenience the neighborhood. To preserve the iron parts of the case from destruction by the vapors, they are repeatedly painted with hot coal tar, care being taken to allow one coat to become thoroughly dry before applying the next one. If the coats are carefully applied and by retouching places which in the course of time show rust spots, the iron is perfectly protected.

In carrying on the operation of nitration, the nitrating vessel is first filled with the appropriate quantity of acid mixture which should be of the same temperature as that usually prevailing in the factory. The cotton, which should be perfectly dry, is then immersed in the fluid and pressed down to accelerate the escape of air.

The proportion between acid and cotton by weight may vary very much, but the nitrating vessel must contain a sufficient quantity of fluid to allow of the cotton being rapidly submerged so that it can quickly absorb the fluid.

But a very short time is actually required for nitration, a piece of fine tissue-paper, for instance, becoming completely nitrated by immersing it for a few seconds only, in a mixture of nitric and sulphuric acids, and then rapidly washing it. It being, however, impossible uniformly to moisten in a short time a larger quantity of cotton, and no disadvantage being connected with the finished gun-cotton remaining somewhat longer in the acid mixture, no general rule regarding the time the cotton is to stay in the fluid can be given, every factory fixing this point for itself. When the cotton has remained for the prescribed time in the nitrating vessel, it is taken out, pressed, or allowed to drain off, and is then thrown into a vessel for the so-called *after-nitration*, which is, however, a misnomer, there being no after-effect of the nitrating fluid. It can only be supposed that the acid still remaining in the pores of the gun-cotton acts upon the portions of cellulose which have escaped its effects while in the nitrating fluid, and converts them also into gun-cotton.

In place of employing the kind of vessels above described, nitration may also be effected in a centrifugal apparatus and the nitrated cotton dried by centrifugal force. The nitrating drum in this apparatus is usually constructed of wrought iron or steel, but these materials being subject to quite rapid wear, drums of aluminium have recently been introduced in some factories, it being claimed that this

metal is capable of offering great resistance to the nitrating fluid.

The perforated drum of the centrifugal is enclosed in a cast-iron jacket, and is impelled from below. During the operation it is closed, the vapors evolved being carried off by a pipe in the lid. The centrifugal is filled four-fifths full with acid mixture and, while slowly revolving the cotton is rapidly introduced, and the acid is for about thirty minutes allowed to act upon it. The acid is then allowed to run off, and the centrifugal is made to revolve very rapidly so that the fluid adhering to the gun-cotton is whirled out, this operation being finished in a short time. The drum is then quickly stopped by means of a brake, and the gun-cotton, which now feels almost dry, is lifted out. The drum can then be immediately used for another operation.

With the use of a nitrating centrifugal, so-called after-nitration is entirely dispensed with, and care must be taken that by the employment of a larger quantity of nitrating fluid, conversion of the cellulose into nitro-cellulose is completed in the centrifugal, this being attained by taking a comparatively very large quantity of the acid mixture for a fixed weight of cotton. In some factories a quantity of acid mixture amounting to two hundred times the weight of cotton is used.

Although nitration is rapidly effected in the centrifugal apparatus, its use is not free from danger, it having been observed that the cotton frequently ignites, this taking place generally towards the end of whirling out. This phenomenon may be explained by the rise in temperature in the cotton when pressed with great force against the circumference of the drum by the rapid revolution of the centrifugal.

When working with the ordinary apparatus, and then leaving the gun-cotton to after-nitration, the operation in the various factories takes from three to twenty-four hours. It is advisable to furnish the vessels used for after-nitration

with perforated bottoms through which the acid draining off from the mass can run off.

WASHING THE GUN-COTTON.

In the further manipulation of the gun-cotton, the fluid contained in its interior has to be removed, and replaced by pure water. Although this operation has the appearance of being very simple, it nevertheless requires close attention, since on the complete removal of the fluid depends not only the stability of the product, but also security in handling and storing it. It happens sometimes that in washing gun-cotton it ignites when introduced into the washing tank, and to reduce this danger to a minimum, the rooms in which nitration and after-nitration are effected should be entirely separated from the wash-room. The vessels used for after-nitration are placed alongside the partition wall through which holes have been cut. In the wash-room, underneath these holes, is an inclined table covered with lead. While one workman lifts by means of a pair of tongs the moist hanks from the vessels and passes them through one of the holes in the wall, another workman draws them from the table and places them immediately in the wash-tank.

The wash-tank consists best of a trough divided in the centre by a board, which, however, should not extend to the ends of the trough. The wash-water flows in from the bottom at one end and runs off through a notch cut in the upper edge of the trough. By this arrangement, the water, together with the hanks placed in it, constantly circulates in the trough, all parts of the gun-cotton being thus brought into intimate contact with it. For the purpose of catching small particles of gun-cotton carried along by the water running off, a basket is placed underneath the notch in the trough.

The gun-cotton remains in the wash-tank until, when rubbed with litmus-paper, the latter no longer reddens.

It is then completely freed from water by whirling in a centrifugal.

If gun-cotton, no matter how carefully washed, be left for some time to itself, it undergoes changes by the acid still remaining in the interior of the cells exerting a decomposing effect. This acid has, therefore, to be removed, which is generally accomplished by boiling or steaming. Boiling is effected in a large vat with a false perforated bottom. The vat having been filled with gun-cotton and water, steam is introduced below the perforated bottom. In some factories boiling is finished in three hours, while in others it is continued for up to three days.

In order to ensure the removal of the acid the water may be mixed with ammonium carbonate, about $\frac{3}{4}$ to 1 oz. per quart of water. Steaming after boiling has been highly recommended for obtaining a product absolutely free from acid. For this purpose the water is discharged from the boiling vat, and steam introduced below the false bottom until it commences to escape in a non-condensed state from the top. It is claimed to have been observed that by long-continued boiling the content of nitrogen in the gun-cotton is decreased, which, of course, must be an injury to it, and that this is not the case in continued steaming.

However, by all these operations the gun-cotton has not been freed from the last traces of acid, and this purpose can only be attained by thoroughly comminuting it in the presence of a large quantity of water. For masses of the fibrous nature of cotton the best apparatus is that known as a beater or hollander used in paper mills for working pulp. It consists of an oblong tank closed on both ends by semi-circular pieces. It is divided by a short, vertical partition into two parts. The floor of one part is sloped and a box of knives is fixed into it. Over this box of knives revolves a cylinder also furnished with knives, and its distance from the lower knives can be regulated at will. By the revolution of the cylinder the water, with which the apparatus is filled, is

constantly kept in a circling motion and the hanks of gun-cotton thrown into the water are drawn between the knives of the revolving cylinder and those fixed in the box, and cut up. As comminution progresses, the cutting cylinder is lowered until the distance between the knives has finally been reduced to fractions of a millimeter.

A certain portion of the gun-cotton is for 4 to 8 hours treated in the hollander, or till the *pulp*—as the comminuted mass is called—has acquired the requisite degree of fineness. It is then tested by taking a sample by means of a ladle from the trough of the hollander, and allowing it to stand quietly for some time. The water is then carefully poured off as long as it is quite clear. Fresh water is then poured upon the sample and after slightly agitating the vessel, the water is again allowed to run off. After this washing operation, nothing should finally remain in the vessel; if there should be a residue of plainly-perceptible, coarser fibres, it is proof of the manipulation of the mass not having been for a sufficiently long time continued. When the mass in the hollander has acquired the proper degree of fineness, it is discharged either by opening a valve in the bottom of the trough, or by sucking off with a pump. The separation of the comminuted gun-cotton from the water is generally effected by means of a centrifugal, the basket of which consists of closely-woven wire lined inside with linen cloths. Some fine particles of gun-cotton being nevertheless carried along with the water, the latter is first allowed to run into a larger vessel, in which the particles of gun-cotton gradually settle on the bottom. The supernatant water is then carefully drawn off.

By treatment in the centrifugal the content of water in the gun-cotton is reduced to about 30 per cent. It is brought into lead-lined wooden boxes and covered with a linen cloth, which keeps out the dust, but does not prevent the mass from drying slowly.

Up to the time the gun-cotton is brought into the store-

boxes the operations are the same, no matter whether an explosive product—actual gun-cotton—or a readily soluble product—collodion-cotton—is to be prepared. For both purposes, cotton perfectly free from water must be used.

DRYING THE GUN-COTTON.

Although gun-cotton can be heated to between 140° and 158° F. without igniting, no factory would dare to run the risk of drying larger quantities of it at such a high temperature, since its explosion might have frightful consequences. Drying even at temperatures below 122° F. is dangerous, dry gun-cotton being a body which becomes highly electric by slight friction, and by a stronger current of air passing over it enough electricity might be generated for a spark to leap over and ignite the entire mass. It is, therefore, necessary to use special precautions in drying gun-cotton.

Drying upon frames covered with linen upon which the gun-cotton is spread out in thin layers, has the appearance of being a very simple process, but, according to Guttmann, it is objectionable, because the gun-cotton is thereby completely insulated, and there is danger of an electric discharge, especially if drying is effected at a higher temperature.

To be entirely secure from an electric tension, Guttmann uses for drying, copper-plates provided with conical openings with a diameter of $\frac{1}{4}$ millimeter on top and of 1 millimeter on the bottom, thus rendering it impossible for them to be stopped-up by the gun-cotton. The copper plates are covered on the edges with leather to prevent friction, and are placed one above the other in the drying room. They are connected one with the other by metallic strips, these conductors being continued into the ground. This arrangement renders an accumulation of electricity in the gun-cotton impossible, any electricity developed being directly conducted into the ground.

Heating the drying room is effected by air being con-

stantly conducted by a ventilator over a system of rib-heating enclosed in a box. The air thus heated passes beneath the drying plates, which are enclosed in boxes, and leaves them heavily loaded with moisture. To prevent heating above a fixed temperature, the drying boxes are furnished with electric thermometers which indicate by ringing a bell when the maximum temperature—which should not be above 104° F.—is exceeded.

Perfectly dry gun-cotton—and this applies also to collodion-cotton—is an exceedingly hygroscopic body, and very rapidly absorbs moisture from the air. It must, therefore, when taken from the drying boxes, be immediately packed in air-tight vessels, bags of rubber or of fabrics impregnated with rubber being used for the purpose. Well-made wooden boxes, the lids of which are made air-tight by rubber strips on the edges, may also be employed. If collodion-cotton has been prepared, it is advisable to dissolve it immediately when it comes from the drying boxes, this having the additional advantage of the solutions, by standing for some time, becoming perfectly clear.

EXPLOSIVE GUN-COTTON.

The effect of highly explosive nitro-cellulose—the actual gun-cotton—intended for blasting purposes, will be the more powerful the smaller the volume into which it is compressed. It is, therefore, made into cylindrical or prismatic bodies of known weight, and the dynamic effect of such a block can at the outset be established. Gun-cotton can only be pressed while in a moist state, and even when subjected to the most powerful pressure always contains a certain amount of water. Its explosive power is, however, not affected by this content of moisture, explosion being brought about by making, while pressing the block, a cylindrical opening in it in which a fuse of dry gun-cotton is inserted.

When gun-cotton is to be compressed, it is stirred with luke-warm water to a thin paste, and in doing this, the pro-

portion of weight of gun-cotton to that of water has to be known. This paste is, as a rule, first freed from the larger portion of water by hand-presses, the shape the finished piece is to have being also given to it.

The article thus preparatively pressed is subjected in hydraulic presses to as strong a pressure as can be produced. The presses must be so arranged that the water pressed out from the mass can escape, otherwise pressure would be ineffective, since fluids oppose great resistance to compression. In the presses variously shaped bodies of gun-cotton are produced, the most common shapes being cylinders or slightly conical pieces, because they can be most readily removed from the moulds of bronze. For certain purposes, for instance, for loading torpedoes, the gun-cotton is compressed in the form of cylindrical segments, which, when put together, make up a slightly tapering cylinder. Smaller pieces similar to the first ones are laid one above the other, a body fitting accurately into the charging space of the torpedo being thus formed. Compressed gun-cotton being very hygroscopic, the compressed articles, when finished, are immediately coated with a water-proof lacquer.

INCREASING THE STABILITY OF THE NITRO-CELLULOSE.

The nitro-celluloses, so far as at present known, belong to the constant combinations, *i. e.*, they remain entirely unchanged in the air or under water, a change taking place only in consequence of an exterior influence. This immutability, however, belongs only to products absolutely free from the slightest trace of free acid, nitro-celluloses which contain free acid, be it never so little, being subject to change, though it may progress very slowly. The change manifests itself first by the originally pure-white mass turning yellowish and acquiring in the course of time a quite dark-brown color, and after a long time, the nitro-cellulose is even converted into a dark-colored, smeary mass. The author of this work noticed, in the course of thirty years,

these phenomena in a small quantity of explosive nitro-cellulose prepared by himself and which was kept in a vessel closed with a ground-glass stopper. Strange to say, on opening the vessel, the mass showed no odor of nitric oxide, and it remained perfectly odorless until it passed into the smeary state. The gun-cotton above-mentioned having only been thoroughly washed with cold water contained probably small quantities of free acid.

According to the process of A. Luck and C. F. Gross, the stability of nitro-cellulose may be increased by treatment with metallic salts, their solutions being allowed to act either directly upon the nitro-cellulose, or with the co-operation of acetone. In the first case, the nitro-cellulose is for 30 to 60 minutes treated in a one per cent. solution of lead acetate or zinc acetate at a temperature of from 176° to 212° F. The nitro-cellulose is then washed until the wash water shows no trace of the metallic salt.

According to the other process, acetone, to which has been added 1 per cent. of its weight of the metallic salt, is poured over the nitro-cellulose, the treatment being, in this case, for half an hour at the ordinary temperature. The fluid is finally drawn off, and the nitro-cellulose thoroughly washed. By both these methods of treatment, a basic salt is claimed to be formed from the residue of acid in the nitro-cellulose with the metal, thus, for instance, of the lead salt up to 2 per cent. of lead oxide being found in the form of a basic combination.

According to O. R. Schulz's process the nitro-cellulose is rendered very stable by bringing it, when freed from acid in the ordinary manner by washing, into a pressure-boiler, together with several times its weight of water, and heating to 275° F. By increasing the pressure up to 5 or 6 atmospheres the operation is in a short time finished, and the nitro-cellulose breaks up to a fine powder, in which form it is especially suitable for the manufacture of cartridges. If heating be effected at as low a pressure as 3 atmospheres—

corresponding to 275° F.—the nitro-cellulose is also rendered stable, but heating has to be continued for a longer time.

The nitro-cellulose thus treated in the boiler is finally washed in cold water for the removal of the soluble bodies. With the use of this process only $\frac{1}{20}$ to $\frac{1}{50}$ of the quantity of water necessary for washing by the ordinary method is said to be required.

SOLUBLE GUN-COTTON OR COLLODION-COTTON.

In describing the preparation of nitrated cotton, attention has been drawn to the fact that there is no fixed boundary between explosive and soluble gun-cotton, but that the latter can be obtained by a suitable change in the proportions of the acid mixture. Experience has shown that this can be best accomplished by using equal parts of sulphuric and nitric acids as nitrating fluid. The nitric acid should contain 75 per cent. of nitric anhydride, and the sulphuric acid 96 per cent. of sulphuric anhydride. The fluid is allowed to act upon the cotton for from 60 to 90 minutes at a temperature of 104° F., and the resulting product is immediately washed.

Collodion-cotton having recently become of great importance for the preparation of textile threads, to which the term artificial silk has been applied, greater demands are now made on it than formerly, when it was chiefly used for photographic and medicinal purposes. For these applications it sufficed for the collodion-cotton to dissolve clear, and, after the evaporation of the solvent, yield a film possessing a certain strength and elasticity.

With reference to the use of collodion-cotton for the manufacture of textile threads of very slight diameter, great value is at present attached to the preparation of a product yielding a solution of great viscosity, the manufacture of very thin threads being only possible with such a solution.

It has been found that the duration of the action of the

acid mixture upon the cotton exerts great influence upon the viscosity of solutions of collodion-cotton. The content of nitrogen is also said to be of considerable importance, though this is disputed by many investigators.

It may here be emphasized that collodion-cotton is never entirely uniform as regards its composition, and that a product of quite uniform general properties can only be obtained by always working with cotton of the same degree of fineness, using an acid mixture of the same composition, and conducting the operation in the same manner as regards temperature and duration of the action of the acid mixture. All these conditions have, therefore, to be taken into consideration in the manufacture of large quantities of collodion-cotton of uniform quality. The manufacturers who require collodion-cotton have determined the correct proportions suitable for their purposes by exhaustive experiments, and if they treat their processes of nitration as secrets, they cannot be charged with assuming an air of mysteriousness.

For the production of collodion-cotton, the solutions of which are to possess a great degree of viscosity, a higher temperature should never be used for nitration, and to prevent a rise in the temperature, it is advisable to place the nitrating vessels in a tank filled with cold water. The process of nitration progressing more slowly at a lower temperature, the cotton is allowed to remain a somewhat longer time in the acid mixture. It is then pressed and immediately washed, the same care being exercised as in washing explosive cotton. The object of comminuting the cotton in the hollander is, in this case, not only to remove the acids, but also to obtain the product in a very finely divided state, it being thus more readily brought into solution.

According to the investigations of G. Lunge and J. Bebie, previously referred to, the solubility of nitro-celluloses is intimately connected with the content of nitrogen in the products; gun-cotton, which contains as much nitrogen as

possible, behaving differently towards various solvents. It dissolves in acetic ether, acetone, benzol and nitrobenzol, but not in nitroglycerine. It is, however, dissolved by a mixture of nitroglycerine and acetone, such a solution serving for the preparation of one of the most effective blasting agents which is known under the name of *blasting-gelatine.*

Complete solubility in a mixture of two parts of ether and one part of alcohol may be considered characteristic of properly prepared collodion-cotton, though there is a product which also dissolves in a mixture of ether and alcohol in which the proportion of the latter is much larger.

If nitro-cellulose be treated at a moderate heat with alcoholic solution of caustic soda or caustic potash, the nitro-combination is in a very short time disintegrated, cellulose remaining behind. This reaction is of great importance for the production of threads and tissues from collodion solutions, as by reason of their great inflammability they would be of no use whatever. However, when treated for a short time with solution of an alkali, they rank, as regards inflammability, with ordinary cotton tissue.

It has from many sides been asserted that a good quality of collodion-cotton can only be obtained by nitrating fine tissue-paper which consists almost entirely of pure cellulose. Direct experiments in this direction have proved that an excellent quality of collodion-cotton can actually be prepared from such paper, it being only necessary for the purpose of nitration, slowly to draw strips of the paper over glass rods placed horizontally in the nitrating vessel and allow them to drain off. If, however, the expense of preparing collodion-cotton from paper is compared with the cost of producing it from cotton, the calculation results in favor of cotton. It may be confidently asserted that all that is necessary is to free cotton from all foreign bodies, *i. e.*, to convert it into pure cellulose, to be enabled to produce from it as good a quality of collodion-cotton as from paper.

COLLODION.

Nitro-cellulose, with a certain content of nitrogen, is capable of dissolving in a number of fluids, and it then forms a viscous mass possessing great adhesive power, to which the term collodion has been applied. When collodion is left to itself until the solvent evaporates, the nitro-cellulose remains behind in the form of a structureless film, which is perfectly colorless, and is distinguished by considerable solidity and high lustre.

Collodion found originally only limited application in the healing art, it being used for the purpose of closing wounds air-tight to prevent the colonization of organisms which cause gangrenous and other complications detrimental to the healing process.

Solutions of nitro-cellulose gained in importance only from the time when the use of collodion in photography became general, and they retained this importance until the photographic process turned more and more towards the so-called dry plates, the sensitized layer of which consists of gelatine. However, collodion regained its great importance by reason of the invention of the preparation of artificial silk, large quantities of it being at present manufactured for this purpose.

In speaking later on of the manufacture of artificial silk, the preparation of collodion for this purpose will be referred to, and only the varieties which are of importance for photographic purposes will here be discussed.

COLLODION FOR PHOTOGRAPHIC PURPOSES.

It has been found by special investigations that a not highly nitrated nitro-cellulose is best adapted for the preparation of collodion for photographic purposes as it dissolves with the greatest ease. Several authors recommend the finest quality of tissue-paper as raw material for its preparation, but the same result is without question ob-

tained by using, in place of this expensive material, a fine quality of purified cotton.

A series of nitro-celluloses is known, the formation of which depends on the action for a varying time of the nitrating fluid and, partially, also on its concentration. According to Eber the composition of these combinations is as follows (the formula for the cellulose having been taken double):

	Content of nitrogen.
1. Cellulose-hexanitrate, $C_{12}H_{14}O_4(NO_3)_6$	14.14 per cent.
2. Cellulose-pentanitrate, $C_{12}H_{15}O_5(NO_3)_5$ . . .	12.75 "
3. Cellulose-tetranitrate, $C_{12}H_{16}O_6(NO_3)_4$	11.11 "
4. Cellulose-trinitrate, $C_{12}H_{17}O_7(NO_3)_3$	9.15 "
5. Cellulose-dinitrate, $C_{12}H_{18}O_8(NO_3)_2$	6.76 "

The cellulose hexanitrate is the insoluble explosive compound which, however, contains always small quantities of soluble substance. Cellulose pentanitrate is soluble in a mixture of alcohol and ether. It is obtained by leaving cotton for several hours (up to five) at the ordinary temperature in contact with a mixture of equal parts of concentrated sulphuric and nitric acids of specific gravity 1.40. The resulting cellulose, as mentioned above, is soluble in a mixture of alcohol and ether, but if the mixture contains only a small quantity of ether, the cellulose pentanitrate alone is dissolved, the admixed tetranitrate and trinitrate remaining undissolved.

Cellulose tetranitrate may be obtained by bringing 0.63 oz. (18 grammes) of tissue paper cut up into thin strips, into a mixture of equal parts of sulphuric acid of specific gravity 1.845 and nitric acid of specific gravity 1.40, and allowing it to remain ¼ hour in the acid mixture, maintaining the temperature during this time at 176° F. The product obtained in this manner is identical with *celloidin*, an article furnished by Scheering's factory at Berlin. Besides tetranitrate, trinitrate is also formed, and the separation of the two compounds is not readily accomplished. The tetra-

nitrate is insoluble in ether as well as in alcohol, but dissolves in a mixture of them, as well as in acetic ether, methyl alcohol, in a mixture of acetic ether and alcohol, and in glacial acetic acid.

Cellulose trinitrate dissolves slowly at the ordinary temperature in absolute alcohol; it is readily soluble in acetic ether, methyl alcohol and boiling glacial acetic acid. A concentrated alcoholic solution acquires a milky appearance by the addition of ether.

Cellulose dinitrate may be obtained in various ways. According to one method, it is formed by allowing highly dilute mixtures of nitric and sulphuric acids to act at a higher temperature upon cellulose until an abundance of red vapors is evolved, and the mass commences to dissolve. Dinitro-cellulose may also be obtained by mixing collodion solution containing 2 to 4 per cent. of nitro-cellulose with a quantity of alcoholic potash lye about three times as large as would be required for the neutralization of the nitric acid present. After one or two hours, the fluid is diluted with water and neutralized with dilute sulphuric acid, a flocculent precipitate being formed, which is carefully washed and dried. It consists of dinitro-cellulose which ignites with difficulty and detonates when heated to 347° F. It is readily soluble in a mixture of ether and absolute alcohol, as well as in absolute alcohol alone, in glacial acetic acid, acetic ether, acetone, and methyl alcohol, but only with great difficulty in pure ether.

The behavior in drying of a solution of dinitro-cellulose in ether-alcohol is of special importance for the preparation of collodion for photographic purposes. By allowing such a solution to evaporate upon a glass-plate, a milky-turbid, soft film is formed which is not transparent, but only translucent. As only a slight admixture of this dinitro-cellulose suffices for collodion to exhibit this phenomenon, this compound has to be considered as entirely unsuitable for the preparation of a good quality of collodion.

For the production of collodion serviceable for photographic purposes as well as for other applications, the collodion-cotton has to be perfectly neutralized. When a sample of the cotton is moistened with water, and after squeezing out the water, litmus paper is reddened by it, the acid adhering to the cotton has to be neutralized. For this purpose the cotton is for half an hour soaked in ammonia diluted with four times its quantity of water, then thoroughly washed, and completely dried upon a plate placed upon a pot of boiling water.

For the preparation of the solution, 50 parts of ether and 50 parts of 95 per cent. alcohol are used for 2 parts by weight of dry cotton. The alcohol is first poured over the cotton, and when the latter has swelled up, the ether is added, solution being accelerated by vigorous shaking. A 2 per cent. collodion is in this manner obtained.

The physical condition of collodion-cotton has a noticeable influence upon its solubility. Pulverulent cotton, which crumbles to dust when rubbed between the fingers, has to be dissolved in a mixture of 40 parts of alcohol and 60 parts of ether, otherwise the resulting collodion layer will not turn out solid.

Collodion solution is best kept in glass bottles of small diameter in a cool, dark place where it is protected from shocks. After standing for some time the undissolved particles of cotton fall to the bottom, where they form a quite heavy deposit, the supernatant fluid being perfectly clear. By carefully tilting the bottles, the clear fluid may be almost entirely poured off.

The preparation of collodion solution for the purpose of manufacturing artificial silk differs in many respects from the process above described, and will be referred to in detail in speaking later on of the manufacture of artificial silk according to Chardonnet.

ELASTIC MASSES FROM NITRO-CELLULOSE (ARTIFICIAL RUBBER.)

A solution of nitro-cellulose in volatile solvents yields, after the evaporation of the latter, a layer of structureless nitro-cellulose, which, however, becomes extremely brittle by drying. This mass may to a certain extent be rendered more flexible by adding to the solution a small quantity of castor oil. The latter is dissolved in strong alcohol, and a quantity of the solution, amounting to about 2 per cent. of the weight of the dry nitro-cellulose, is added to the collodion.

The castor oil, after the evaporation of the solvent remaining, uniformly distributed throughout the nitro-cellulose, imparts to the latter a certain degree of flexibility, and prevents thin layers of the mass from becoming brittle, without, however, conferring upon them a higher degree of elasticity.

For the production from nitro-cellulose of masses possessing considerable elasticity other means have to be adopted. The nitro-cellulose has to be dissolved in fluids having a high boiling point, and which consequently do not evaporate in the air, but impart to the mass a soft, elastic property similar to that of collodion still containing remnants of the solvent.

The following fluids possess these properties and are at the same time capable of dissolving nitro-cellulose: Nitrobenzol, nitrotoluol, dinitrotoluol, nitrocumol, nitronaphthalin, etc. However, their use in practice is almost out of the question because they are too expensive.

A uniform mass may, to be sure, be produced by bringing dry soluble nitro-cellulose in contact with one of these solvents or a mixture of them; but long-continued manipulation is required. The object may, however, be attained in a more simple manner by first dissolving the nitro-cellulose in one of the volatile solvents ordinarily used, then adding one of the above-mentioned less volatile solvents, and allowing the volatile solvent to evaporate.

For this purpose it is not necessary to prepare an entirely clear solution of nitro-cellulose in a volatile solvent, only enough of the latter being used to cause the nitro-cellulose to swell up so that a mass resembling very thick glue solution is formed.

A kneading apparatus allowing of thorough mechanical manipulation is used for preparing the mass. Since during this manipulation, the volatile solvent would evaporate, the kneading apparatus should be placed in a box which can be closed air-tight, and provision must be made for a contrivance by means of which a current of warm air can be passed through the apparatus.

The nitro-cellulose having been introduced, the apparatus is closed, and the necessary quantity of solvent admitted. The most suitable solvent is a mixture of equal parts of ether and alcohol, though acetone or methyl alcohol may also be used. The mixing contrivance is then set in motion and kept going until the contents of the apparatus have been converted into a uniform mass in which no lumps of swollen, undissolved nitro-cellulose are noticed. The heavy volatile solvent is then introduced, and the mixing apparatus kept constantly in motion until the mass has again become homogeneous. This is the period at which the greater part of the volatile solvent may be regained by distillation.

For this purpose a current of warm air is passed through the apparatus, and, when loaded with the vapors of alcohol and ether, is conducted through a cooling pipe in which the vapors are condensed. However, the entire quantity of volatile solvent must not be distilled off, otherwise the mass in the apparatus would become so viscous as to clog the kneading contrivance.

The further manipulation of the mass is effected by rolls, the rest of the volatile solvent still contained in it being thereby completely evaporated. Rolling has to be several times repeated to make the mass thoroughly homogeneous.

The nature of the masses finally obtained depends on the proportional quantities of nitro-cellulose and solvent. The more of the latter is present the more elastic the masses will be, and by a suitable change in the proportions, masses almost equal, as regards softness and elasticity, to a fine quality of rubber may be obtained. The smaller the quantity of solvent, the more solid and harder the resulting masses will be.

These masses, when heated, acquire a higher degree of stablity, and can then by pressure be brought into any shape desired, and as they can be readily mixed with indifferent bodies, articles of very varying appearance may be made of them. For mixing purposes, powders of cheap, indifferent bodies, such as chalk, asbestus, talcum, etc., are especially suitable. If other than white masses are to be prepared, any desired coloring matter may be mixed with the white powders, colored masses of very neat appearance being thus obtained. On account of their great elasticity, the term *artificial rubber* has been applied to these peculiar nitro-cellulose masses, and for many purposes they may serve as substitutes for rubber.

The above-described masses, consisting as they do largely of nitro-cellulose, are quite inflammable, without, however, exhibiting any explosive properties. The inflammability, however, becomes less with the use of a larger quantity of indifferent substances, it being thereby actually reduced to a very slight degree, and it may be still further decreased by superficially denitrating the finished articles. This is accomplished by dipping them for a short time in hot soda lye, the outer layers of nitro-cellulose being thereby converted into cellulose. An article thus treated will not ignite, even when brought in contact with a red-hot body, the point of contact being simply blackened by the carbonization of the outer cellulose layers.

The elastic nitro-cellulose masses prepared according to the process above described, are by many investigators con-

sidered as deserving the greatest attention of all the bodies which have been proposed as substitutes for rubber, they approaching nearest, as regards their properties, the genuine article, without, however, being capable of entirely replacing it.

CELLULOSE ESTERS.

In addition to the esters yielded by cellulose by the action of nitric acid, analogous combinations with other acids may be prepared. But a small number of combinations belonging to this series are at present known, but it may be supposed that many of them may in the future acquire a certain importance for the industries. It has, therefore, been considered advisable to give a few facts regarding the nature and preparation of these combinations.

CELLULOSE ACETIC ESTER.

Cellulose tetra-acetate or cellulose acetic ester is prepared, according to Henckel–Donnersmark's process, from a molecular mixture of cellulose and magnesium acetate, and, therefore, 630 grammes (21.87 ozs.) of magnesium acetate have to be used for every 720 grammes (25.39 ozs.) of cellulose, pure cellulose prepared from cellulose sulphocarbonate being said to be especially suitable for preparing the combination. The above-mentioned mixture of cellulose and magnesium acetate is intimately mixed in a kneading machine, the mixing vessel of which can be heated, with 810 grammes (28.57 ozs.) of acetyl chloride and 450 grammes (15.87 ozs.) of anhydrous acetic acid. When the chemicals commence to act one upon the other 4.5 liter (4.65 quarts) of nitrobenzol are added in very small portions at a time, a fresh quantity being only added when the previous one has been completely taken up by the mass. The addition of the nitrobenzol is so managed that about one-half of it remains when the temperature of the mass has risen to 158° F. This quantity is then at one time brought into the mixing vessel, and the mixing machine

kept going for three hours longer. A thinly-fluid solution of the tetra-acetate still containing traces of unchanged cellulose and of lower acetates is thus obtained.

The warm solution is poured into 22.5 liter (23.76 quarts) of alcohol, the acetate precipitating thereby as a white, finely-flocculent mass, which is separated from the fluid by filtration. This flocculent mass is washed with warm alcohol, the washing fluid is added to the mother-lye, and the flocculent mass subjected to strong pressure. It is then, without previous drying, comminuted, stirred together with water, and boiled in the latter until the last traces of the solvent have been evaporated. The mass is then again filtered, washed first with warm water acidulated with a small quantity of hydrochloric acid to remove the last traces of the magnesium salt, and then with pure warm water, until the fluid running off shows a neutral reaction. It is then again subjected to pressure and finally dried at a temperature not exceeding 176° F. Of the homologues of nitrobenzol, Henckel-Donnersmark has used with equal success o-nitrotoluol, p-nitrotoluol, o-nitro-ethylbenzol and the nitroxylols and nitrocumols from isopropyl-benzol.

The composition of cellulose tetra-acetate corresponds to the formula $C_6H_6O_5(C_2H_3O)_4$. The combination is insoluble in methyl alcohol, ethyl alcohol, ethyl acetate, amyl acetate, acetones and ether; it dissolves in ethyl-benzoate, chloroform, glacial acetic acid and nitrobenzol. The solution in nitrobenzol congeals on cooling to a solid, perfectly transparent jelly.

When a solution of cellulose tetra-acetate is poured upon a glass-plate and allowed to evaporate, the combination is left behind in the form of laminae of extraordinary transparency which show considerable solidity even when just of such a thickness as still to exhibit the iridescence of very thin layers. Towards the action of chemicals, the combination shows a degree of indifference which considerably surpasses that of nitro-cellulose, it being not attacked by

alkalies, which produce no effect whatever even at a higher temperature. The combination is only destroyed by boiling it for several hours in alcoholic soda lye, cellulose remaining behind which, however, retains the form of laminae, as well as the transparency.

One property of the combination which may perhaps become of great technical importance, is its insulating power, which is better than that of rubber or gutta-percha. The acetate softens only at about 302° F., and is not inflammable.

The great chemical indifference of this substance and its extraordinary insulating power may secure for it considerable application in the electrical industry. For many purposes it might also serve as a substitute for celluloid, especially in cases where the use of this material is excluded by reason of its great inflammability. Since, as previously mentioned, very thin, but nevertheless very solid, laminae can be obtained by the evaporation of dilute solutions of the ester, such solutions might prove very suitable for lacquering metals to protect them from atmospheric action.

According to L. Lederer an acetyl derivative of cellulose is prepared by bringing hydro-cellulose in contact with sulphuric acid and acetic anhydride at a temperature, which should not be much above 158° F., the process being as follows: The cellulose is allowed for a few minutes to remain in contact with dilute (3 per cent.) sulphuric acid. It is then pressed out, dried and heated for three hours at 158° F. Four times the quantity of acetic anhydride is then poured over it. A vigorous disengagement of heat immediately takes place, and the heat in the interior of the closed vessel must be so moderated by cooling that it does not exceed 158° F. The hydro-cellulose is gradually dissolved and when reaction is complete, the mass is mixed with water, thoroughly washed, and dried.

The acetylated cellulose thus obtained forms a white powder of a gritty nature, soluble in chloroform or nitro-

benzol. According to Lederer, the acetyl-cellulose prepared in the manner above described, is especially suitable as a substitute for collodion, and for the preparation of articles resembling celluloid in appearance, but distinguished from it by being perfectly free from odor and not being inflammable.

Lederer has later on modified his process by submitting the mass, after adding the acetic acid, to uninterrupted mechanical manipulation, the temperature, by constant cooling, being prevented from rising above 86° F. The mechanical manipulation is continued until the mass presents the appearance of transparent paste, when, by the addition of water, the acetyl-cellulose is separated and further worked.

CELLULOSE BUTYRIC ESTER.

Cellulose tetra-butyrate or cellulose butyric ester is prepared in a manner analogous to the acetate, and, as regards its properties, closely resembles the latter, but is distinguished from it by being more readily soluble in the solvents above-mentioned, and dissolving also in ethyl acetate and in acetone. Laminæ obtained from the butyrate by allowing solutions of it to evaporate, are somewhat softer and more flexible than laminæ from the acetate.

In addition to the above-mentioned esters, Henckel–Donnersmark has prepared a series of similar combinations, for instance, the double ester—cellulose aceto-butyrate—further, cellulose palmitate, cellulose phenyl-acetate, etc. As regards their properties, these combinations show a certain resemblance to those previously described. Thus far, no application of them in the industries has become known.

"SOLID SPIRIT."

A peculiar use is made of cellulose acetate, according to statements by the "Farbenfabriken," formerly Fr. Boyer & Co., for the purpose of bringing alcohol into a solid form—

solid spirit. For the preparation of this peculiar product, 100 grammes (3.52 ozs.) of cellulose tri-acetate are dissolved in 500 grammes (17.63 ozs.) of glacial acetic acid and the solution is quickly brought into 2 liters (2.113 quarts) of alcohol. Cylindrical structures of a gristly nature are formed from which the excess of glacial acetic acid and alcohol is removed by pressure. They are then dried in the air and kept in closed vessels for use. When heated the product does not melt, and when ignited, burns uniformly without leaving a residue.

IX.

ARTIFICIAL SILK.

The substance to which the general term *silk* has been applied is the product of the larvæ or caterpillars of different Lepidoptera of the genus *Bombyx*, and of a few other varieties. When the larva has attained its period of full growth, it contains in large vessels, almost occupying its entire body, a glutinous fluid which is either colorless or yellow, or sometimes orange-red. These vessels are by means of very small apertures connected with a spinner on the posterior of the larva, and while the latter spins its cocoon the glutinous fluid passes in unbroken lines through the apertures of the spinner.

The glutinous fluid immediately coagulates under contact with air to a very thin thread, which is either colorless, yellow or orange-red, and represents the raw silk. However, the latter does not consist of a uniform mass, but of two distinct bodies. The outer layer is gelatinous and gummy, forming the so-called silk-glue, and has to be removed previous to the further manipulation of the raw silk. The core enclosed by this outer layer is the actual silk substance, or sericin, or fibroin. In addition to these substances, several other bodies, such as albumen, coloring matter, wax and fat, occur in silk. The composition of raw silk is, therefore, quite complex, and consists, as a rule, of 20 per cent. of the gelatinous substance; 53 per cent. of actual silk substance or sericin; 24 per cent. of albuminous combinations, and 3 to 4 per cent. coloring matter, fat and wax.

By a special operation, called scouring or boiling, the raw silk is deprived of all other substances except the seri-

cin or fibroin, when it can be further worked by mechanical means. This operation is generally effected by repeatedly boiling the raw silk with soap solutions.

Viewed under the microscope, a thread of silk freed from its envelope of gummy matter appears as a massive cylinder (without cavity), resembling in its appearance a glass rod, and showing here and there very slight cross-stripes. The diameter of the individual threads is very slight, varying according to the degree of fineness of the silk between $\frac{1}{26}$ and $\frac{1}{40}$ of a millimeter. Notwithstanding this slight thickness, silk threads possess an uncommonly high degree of strength and elasticity by far surpassing in this respect all other textile fibres.

Silk being not available in unlimited quantities and the demand for it being constantly on the increase, chemists have for a long time endeavored to produce it by artificial means, but the results have always proved unsatisfactory. However, efforts to obtain masses for the production of threads which, as regards fineness and lustre, closely resemble actual silk and can be spun and twisted, have been more successful, but none of these substitutes for silk can, as regards strength and elasticity, compare with the natural product, even the best of them being in this respect far inferior to it.

VARIETIES OF ARTIFICIAL SILK.

Three varieties of silk-substitutes or *artificial silk* may at present be distinguished and according to their origin may be designated as *cellulose-silk*, *collodion-silk*, and *glue- or gelatine-silk*.

As the matter stands at present, pre-eminence above all other substitutes has to be given to collodion-silk, while glue-silk decidedly occupies the lowest place. However, cellulose-silk might in the future take precedence over collodion-silk, it possessing decided advantages over the latter.

With reference to the historical development of the artificial silk industry, the French chemist M. de Chardonnet was the first to occupy himself successfully with this subject. As early as 1884 he deposited with the French *Académie des sciences* a sealed document, which was opened November 7, 1887, and bore the title *Sur une matière textile artificielle resemblant à la soie* (on an artificial textile substance resembling silk).

The process for the production of a textile substance resembling silk suggested, in 1889, by Du Vivier, and designated by him as *soie de France*, can only be considered a modification of Chardonnet's method. Du Vivier, as well as Lehner, uses solutions of nitro-cellulose for the production of textile threads, this being also the pith of the first invention, collodion being Chardonnet's initial material.

Lehner also starts off with nitro-cellulose, but employs for its solution substances differing from those used by Chardonnet, and mixes this solution with silk-fibroin prepared from silk waste, or with solution of artificial rubber prepared from drying oils. The fluid pressed into the form of a thread is conducted into a bath of oil of turpentine, or of a mineral oil, in which it coagulates, and the thread thus obtained, which is still soft and viscous, is stretched previous to being reeled up.

A. Millar utilizes for the production of textile threads the property of glue solution mixed with potassium dichromate, becoming insoluble on exposure to light. For this purpose a clear solution of gelatine is mixed with solution of potassium dichromate, the solutions being prepared in the proportion of 100 parts of gelatine to 2 or $2\frac{1}{2}$ parts of potassium dichromate. The fluid should only contain sufficient water to emerge from the narrow spinning apertures in the form of a viscous thread, which on exposure to light becomes insoluble.

Hummel, of Leeds, converts pure gelatine solution into threads, dries them and prepares from 16 to 18 such

threads, skeins, which are exposed to the vapors of formalin, whereby the gelatine is deprived of its solubility in water.

Comparative experiments have shown that threads prepared from glue (gelatine) possess a comparatively high degree of brittleness, and in addition have the very disagreeable property of swelling up very much in moist air.

Cadoret uses in his method an intermediary between Chardonnet and Millar's processes. He dissolves dinitro-cellulose in a mixture of ether and acetic acid, and mixes this solution with glue solution or albuminous substances, so that a fluid is formed which can be drawn out to thin threads. The latter acquire solidity by being drawn through a tannin solution, by which the glue substance or the albumen is transformed into an insoluble body. The thread obtained by this process consists, therefore, of a mixture of dinitro-cellulose and the combination of tannin and glue, or albumen.

The methods according to which textile threads are prepared from pure cellulose instead of nitro-cellulose differ essentially from those mentioned above. Several processes in this direction have become known, each of which may, however, be considered as original, though of greatest importance is perhaps the method according to which a solution of cellulose in cuprammonium is prepared, and the cellulose again separated in the form of fine threads. Several such processes for the preparation of textile threads from cellulose are known, but only one of them has thus far been permanently introduced in practice, this being the invention of Dr. Hermann Pauly, of Gladbach, which is at present carried on on a large scale. A process in which the use of nitro-cellulose is also avoided has been proposed by Langhaus. It consists in the main, in kneading cellulose with sulphuric and phosphoric acids into a doughy mass, which is diluted with sufficient phosphoric acid to form a viscous mucilage capable of being spun. No particulars of the availability of this process on a large scale are known,

but it will very likely not become of practical importance, if for no other reason than that in cuprammonium and viscose we have materials which allow of a more easy manipulation of the mass than is the case when highly concentrated acids have to be used for its preparation.

By reason of its cheapness and safety, an excellent method for the preparation of silk-like threads is the one in which viscose solution is used, it being possible, even at the present state of the process, to produce textile threads which, as regards beauty, are not inferior to Chardonnet silk. From the present state of the manufacture of textile threads by artificial means, it would seem very probable that Chardonnet's process can gain a permanent position in practice only when the skeins can be successfully deprived of their great inflammability. As regards the methods in which cellulose solutions are worked, the process in which cuprammonium is employed as solvent, as well as the one with viscose, appears to have a great future before it.

It may here, however, be most emphatically stated that for all that, the services rendered by Chardonnet in creating this entirely new branch of industry are not the less great, because he not only made the first suggestions, but perfected the mechanical part of the entire manufacture so that, in this respect, the work of all inventors after him has been essentially facilitated.

CHARDONNET ARTIFICIAL SILK.

According to Chardonnet's original patent, the process of preparing textile threads is as follows: One hundred grammes (3.52 ozs.) of pyroxylin together with 10 grammes (0.35 oz.) of a reducing metallic protochloride, such as protochloride of iron, chromium, manganese or tin, and 0.2 grammes (3.08 grains) of an oxidizable base, such as, for instance, quinine, aniline or rosaniline, are dissolved in a mixture of 40 parts of ether and 60 parts of alcohol, and a coloring substance is added to the warm solution. This

fluid is pressed through a narrow tube, which is surrounded by cold water. The thin thread thus obtained coagulates immediately on the surface, while the interior still remains liquid. Hence, previous to complete coagulation, this thread may be stretched, and this is done so far as the tenacity of the substance will permit without tearing the thread. The finished thread is then dried and reeled up.

Based upon this method, the merest outlines of which are given above, several factories are at present working in France, and in Switzerland, and one in England, and the establishment of others is said to be in contemplation.

Regarding the practical application of Chardonnet's process, the following details have become known:

Perfectly pure cellulose always serves as raw material, and cellulose of any derivation may be used, provided it has been sufficiently purified. However, it has been shown by comparative experiments that the product obtained from cellulose prepared from wood is far inferior to others as regards purity and beauty of the white color, as well as tenacity. Hence in factories working according to Chardonnet's process, pure cotton is used as the starting point in the manufacture. The cotton is first carefully cleansed by mechanical means and then further chemically purified by weak alkaline solutions, so that it may be considered pure cellulose. It is finally loosened up in a carding machine, and then subjected to nitration.

NITRATION OF THE COTTON.

The nitrating fluid is prepared from nitric and sulphuric acids, great importance being attached to its being always of exactly the same composition. This also contributes to the nitro-cellulose showing at all times the same composition, which is still further promoted by constantly executing all the operations during nitrating according to exactly the same plan.

Fifteen parts of fuming nitric acid, of 1.52 specific gravity,

and 85 parts of sulphuric acid are used. The mixture is prepared in the morning, and such care is exercised that even the content of moisture in the air of the previous night is taken into consideration, because in damp nights the sulphuric acid absorbs somewhat more water than in dry nights; hence, in the first case, a somewhat larger quantity of sulphuric acid has to be taken.*

Stone-ware pots, each holding about 40 quarts, are used for nitrating vessels, and 8.8 lbs. of dry cotton are brought into each pot, and 35 quarts of acid mixture are immediately poured over them. The pots are placed under a contrivance for carrying off the vapor evolved. Immediately after the acid mixture has been poured over the cotton, the contents of the pot are thoroughly stirred, so that all portions of the cotton become completely moistened with the fluid. The pots are then covered with glass plates.

The time during which the cotton remains in contact with the acid depends materially on the temperature of the air. It is also stated that the content of moisture in the air is also of influence, but this appears not quite clear because gases endeavoring to escape outward hang constantly over the fluid in which the cotton is immersed and, furthermore, the pots are covered with glass plates. If the content of water in the acid has been too large, the nitrated cotton does not completely dissolve, and if the temperature has been too high, a portion of the cotton is entirely destroyed. To obtain a thoroughly uniform product it would, therefore, seem advisable always to use an acid mixture of one and the same temperature and to place the nitrating vessels in a large holder in which a strong current of cold water constantly circulates. By working in this manner there will be no difficulty, after a few experiments, to determine ac-

* If the sulphuric acid be kept in vessels closed air-tight, moist air exerts no influence whatever upon it, and it would seem that these statements are only made for the purpose of representing to the public the manufacture as a matter of particular difficulty.

curately, within a few minutes, the time required for nitration. (Compare as regards this subject, the investigations of G. Lunge and J. Bebie previously referred to.)

When nitration has been correctly carried on, the structure of the cotton shows no change, it being only somewhat coarser to the feel and more brittle. The physical behavior of the nitrated cotton exhibits, however, a very essential change, especially as regards its behavior towards polarized light, which is closely connected with the degree of nitration, though the latter may also be established by the direct determination of the nitric oxide formed from a weighed quantity of nitro-cellulose. However, the physical examination being less troublesome and, what is the main point in this case, requiring but little time, the degree of nitration is determined with the assistance of the polariscope. Chardonnet, in compiling a series of comparative experiments in the chemical and optical way, arrived at the following results:

1. Nitration has progressed to the formation of cellulose tetranitrate, corresponding to the development of 110 cubic cm. nitric oxide from every 1 g. of nitrated cotton. At this stage nothing striking is seen in the polariscope except a few large fibres of a shriveled-up appearance.

2. The polariscope shows the above-mentioned fibres to be present in larger numbers and already mixed with iridescent fibres. The product yields 145 cubic cm. nitric oxide, and is cellulose hexanitrate. From 146 cubic cm. nitric oxide up, the fibres become more uniformly gray, this continuing to 160 cubic cm.

3. From 160 cubic cm. on—cellulose heptanitrate being now present—up to 180 cubic cm., the color, when the mass is tested in the polariscope, turns from straw-yellow to orange-red.

4. When the quantity of nitric oxide evolved becomes greater than 160 cubic cm., the mass is first colorless, then violet, dark-blue and pale-blue, the latter color becoming

the more pronounced the further nitration progresses. When, in polarized light all the fibres appear uniformly of a pale-blue color, it is an indication of nitration being complete.

The cotton is then lifted from the nitrating vessel, allowed to drain off, and the adhering acid removed by means of a hydraulic press. The acid thus recovered is mixed with an adequate quantity of fresh acid and again used for nitration. The manipulation in the hydraulic press, of the nitrated cotton, saturated with acid, creates difficulties in so far that the metal parts of the press are strongly attacked. This is prevented by coating them with lead, plates of the same material being also used for covering the floors of the rooms in which acid is handled.

The gun-cotton comes from the hydraulic press in the form of solid cakes, which are immediately comminuted in the hollander, and washed. The hollander most suitable for this purpose is furnished with a horizontal shaft around which stirring paddles revolve. The size of the machine should be such that 88 lbs. of dry material, as it comes from the press, can at one operation be worked.

Washing the nitrated cotton is an operation of great importance, the last traces of acid having to be removed by it. The washing process requires from 10 to 12 hours, and during this time the water has to be changed up to sixteen times, 22 gallons of water being calculated on for every 2.2 lbs. of dry material.

The nitro-cellulose having been sufficiently washed is returned to the hydraulic press, and its content of water reduced by pressure to 36 per cent., it remaining in this condition until after it is spun, when it is completely dried. This high content of water renders it perfectly safe, and for further working it is simply kept in vessels protected from dust.

PREPARATION OF THE COLLODION SOLUTION.

The solution of the nitro-cellulose in the mixture of

alcohol and ether is effected in a horizontal iron cylinder lined with tin, and capable of revolving around its longitudinal axis. A mixture of equal parts of 95 per cent. alcohol and ether is used as solvent, and about 100 quarts of the mixture are employed for every 48.4 lbs. of dry nitro-cellulose.

The vessel containing the nitro-cellulose and the solvent is uninterruptedly kept slowly revolving by means of a mechanical contrivance until solution is complete, the time required being from 15 to 20 hours. A small quantity of the fluid is from time to time taken from the vessel by means of a test-cock, and when it appears perfectly clear, without any turbidity caused by minute flakes, the solution is of the proper quality.

However, the viscous solution nevertheless contains undissolved or incompletely-swollen fibres imperceptible to the naked eye, by which the production of an entirely uniform thread in any desired quantity would be rendered impossible. For the removal of these minute fibres the solution has to be filtered. However, with a fluid of the viscous nature of nitro-cellulose solution, this operation can only be effected with the use of very strong pressure upon the surface of the fluid, a pressure of 30 to 60 atmospheres being, according to experience, required for the purpose.

The filtering contrivance consists of a cylindrical vessel, the filtering material being placed upon the bottom, a layer of fine cotton wadding, 0.39 to 0.59 inch thick, being used for the purpose. This layer of cotton wadding is enclosed between two sheets of finest silk gauze, and covered on both sides with tinned metallic cloth. The filter has a capacity of about 100 quarts of nitro-cellulose solution, and having been charged with fluid and closed, air under pressure is introduced through a pipe on the top, the pressure being gradually increased to such a degree as required to cause the filtered fluid to run off in a sufficiently thick stream.

Before being further worked, the filtered fluid is for a

certain time kept in glass carboys, each holding about 50 quarts, it having been shown by experience that, as regards its capacity of being spun, it thereby gains considerably in quality. The cause of this phenomenon is very likely found in the fact that during storing, a thorough intermixture of all the particles of fluid takes place so that the smallest differences in the quality of the separate portions of fluid are removed. Hence, in order to have constantly collodion of the best quality, a certain quantity should always be kept on hand, so that it may be stored for a sufficiently long time previous to being spun.

SPINNING THE COLLODION.

For the production from the perfectly homogeneous collodion of a thread representing artificial silk, an apparatus has to be used, which is furnished with extremely narrow apertures through which the collodion solution is pressed. The thread suspended free in the air yields, by evaporation, the ether and alcohol, and is in a short time changed to a solid thread, which, however, still possesses sufficient elasticity and plasticity to allow of its being drawn out by slight tension to a still thinner thread, which is then reeled up and further worked.

For the production of the thin threads, sieve-like metal plates may be used, or, what would appear more suitable, narrow glass nozzles. The disposition of the spinning apparatus used in factories arranged according to Chardonnet's system is as follows:

The collodion to be worked is contained in a vertical, tin-lined steel cylinder, provided on top with a pipe through which air under pressure may be introduced. To the lower end of the cylinder is secured a steel pipe furnished with glass spinners placed at a distance of about 0.78 inch one from the other.

The glass spinners are made by drawing out glass tubes over a glass-blower's lamp, so that the lower opening has a

diameter of only $\frac{1}{800}$ millimeter. The uniformity of the threads being, of course, dependent on the aperture of all the spinners having the same diameter, great care has to be exercised in their manufacture. Every finished spinner must be examined, as to its diameter, with the microscope, and only those are available which by microscopical measurement show uniformity of diameter, all others with wider or narrower apertures being rejected as useless.

The spinners of proper diameters are cemented in a metal frame and, together with the latter, secured to the horizontal pipe of the apparatus. By gradually increasing the air-pressure upon the surface of the collodion, it is finally increased to such a degree that the collodion is with the proper velocity pressed from the spinners. The pressure required for this purpose depends on the viscosity of the collodion, and ranges from 40 to 50 atmospheres.

The spinning apparatus was originally so arranged that the fine threads pressed from the spinners passed into water mixed with $\frac{1}{2}$ per cent. of nitric acid. However, this was found to be entirely superfluous; the threads could be directly worked as they came from the spinners, coagulating almost immediately under contact with air. With the assistance of contrivances closely resembling the reels on which natural silk is wound from the cocoons, the threads are caught and reeled up. A counter records the number of revolutions made by the reel, and the diameter of the latter being known, the length of thread, after the reel has revolved for a certain time, is also known. In this manner an unbroken thread many thousand meters long may be produced, but, as a rule, only 500 meters (546.81 yards) are wound on one reel, when the thread is taken off and brought together to a skein.

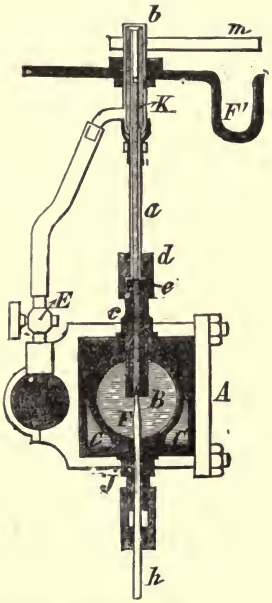
By the solidification of the threads, the total quantity of alcohol and ether contained in the collodion passes in the form of vapors into the air. For the removal of these vapors the spinning room should be provided with a very

powerful airing contrivance by which the air loaded with vapors is carried off and replaced by fresh air from the outside. For this purpose a suitable number of electrically-driven ventilators revolving with great rapidity are, as a rule, fixed in the ceiling of the spinning room.

THE SPINNING APPARATUS.

The main features of the arrangement of Chardonnet's spinning apparatus are shown in Figs. 34 and 35. The narrow glass tubes *a*, which serve as spinners, are sur-

FIG. 34.

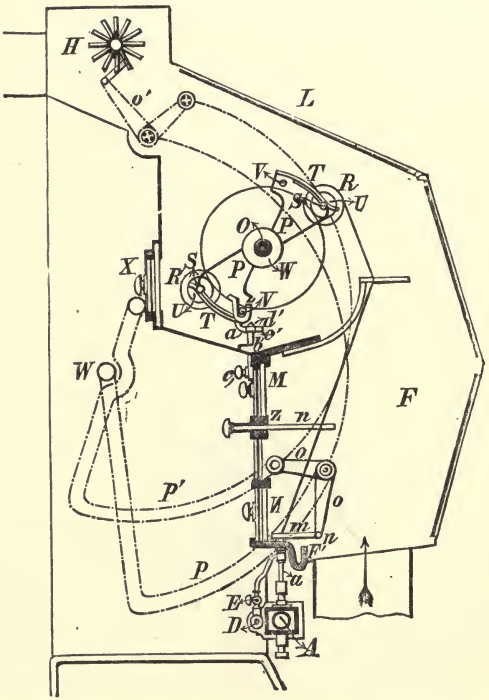


Chardonnet's apparatus for the preparation of artificial silk.

rounded by a pipe, *K*, filled with water, and are fixed upon the joint pipe, *B*, which is surrounded by two channels, *C*, in which hot water circulates. The lower aperture of each spinner is surrounded by two curved spring-blades which form pincers, *m*. By means of the joint lever *o* and the

curved arms *p p*, these pincers oscillate constantly up and down over the reels or spools on which the threads are wound, so that in case one of the threads should break, it is immediately caught by them and returned to the reel or spool. So long as the thread runs without breaking, the pincers move up and down empty. The revolving brush, *H*, cleans the pincers on the upper end of the lever.

Fig. 35.



Chardonnet's apparatus for the preparation of artificial silk.

The spindles of the spools, *R*, which serve for winding up the threads just spun, sit upon the loose cheeks of the revolving axle *o*. They carry small rolls *V*, which are in contact with the surface of smaller sheaves *A*. By this arrangement the simultaneous revolution of all the spools is secured, and

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the cheeks for replacing the full spools with empty ones are also simultaneously moved. The entire spinning apparatus is enclosed in a glass case, *L F*, through which a current of warm air is constantly passed for the purpose of forcing the vapors of alcohol and ether to the condensing vessels.

The first of these condensing vessels contains a solution of soda in water upon which the condensed alcohol floats. The vapors escaping from this vessel hold much ether, but very little alcohol, and are conducted through several vessels containing sulphuric acid which absorbs the total quantity of vapors. This sulphuric acid is utilized for the preparation of ether.

The threads obtained in the manner above described consist of nitro-cellulose, to which, however, still adheres almost the entire quantity of water (about 36 per cent.) originally remaining in the pressed nitro-cellulose. This content of water is left in the threads till they are finished to prevent otherwise possible spontaneous ignition.

The next step in the operation consists in throwing or twisting the individual threads, and finishing them by drying. The latter operation is effected by taking the thrown threads from the reels and passing them through a room the temperature of which is kept at 113° F. While the threads pass through this room all the water still adhering to them is evaporated, complete drying being insured by keeping up, in addition, a strong current of air during the quite rapid passage of the threads through the room.

Notwithstanding its beauty, the artificial silk thus obtained would not be of any practical use if it were left in this condition. It consists of nitro-cellulose and being, therefore, highly inflammable, a fabric made of it would in an infinitely short time be reduced to ashes by a spark falling upon it. The artifical silk is therefore subjected to an operation to which the term *denitration* has been applied, its object being to reconvert the nitro-cellulose into ordinary cellulose.

This denitration constitutes one of the most difficult portions of the manufacture of artificial silk, because it has to be done as completely as possible, without, however, impairing in the slightest the lustre and smoothness of the threads.

Denitration may be effected by conducting the threads of nitro-cellulose through solutions of alkaline sulphides, and the sulphides of potassium, sodium or ammonium may be used for this purpose. However, ammonium sulphide seems to be most suitable, it causing very complete denitration without attacking the silk itself. The different factories keep the composition of the fluids used by them for denitration secret, but a fluid of the proper quality may be readily prepared with the use of ammonium sulphide obtained by saturating concentrated ammonia with sulphuretted hydrogen, and allowing it to stand until it has become yellow. Ammonium sulphide which has turned yellow contains the polysulphides of ammonium in solution, and they appear to be especially effective in denitration.

The ammonium sulphide obtained in the above manner is, of course, too concentrated for use, and to obtain a denitrating fluid of the proper quality, fluids consisting of water to which a certain percentage of concentrated ammonium sulphide has been added, must be employed. The operation has also to be effected at a certain temperature, denitration taking place much more rapidly at a higher temperature than at one but a few degrees lower.

The correct composition of the denitrating fluid may be recognized, on the one hand, by the appearance of the denitrated threads under the microscope; they should, after denitration, be as smooth, uniform and lustrous as before. If the fluid has been too concentrated and acted too vigorously, it is immediately recognized by the appearance of the threads under the microscope; they are lustreless, dull and here and there even corroded. The correct composition of the denitrating fluid may, on the other hand, also

be established by chemical analysis, which should show that the silk contains no nitric oxide whatever, or that the quantity of its content has been reduced to a minimum.

By denitration the silk acquires a yellow color and has therefore to be subjected to a bleaching process, a small quantity of chloride of lime and hydrochloric acid being used for the purpose. In factories working according to Chardonnet's system, 400 grammes (14.11 ozs.) of chloride of lime and 800 grammes (28.21 ozs.) of hydrochloric acid for 16 kilogrammes (35.2 lbs.) of artificial silk are found sufficient.

The bleached skeins of silk are freed by careful washing from adhering bleaching agent, then, as far as possible, dehydrated in a centrifugal, and finally dried. The product thus obtained is of a pure-white color, has the feel of natural silk, but surpasses the latter in beauty of lustre.

PREPARATION OF COLORED ARTIFICIAL SILK.

Colored artificial silk may be prepared in two different ways, namely, by direct coloring while preparing it, or by dyeing the finished skeins. The first-named process has the appearance of being the more simple one, thus deserving the preference, but it has been learned by practical experience that the more suitable way is to prepare first the white silk, and then follow the same method used in dyeing natural silk.

Dyeing the artificial silk while in the course of preparation is effected by simply dissolving the coloring matter in the collodion, the readily soluble aniline colors being, by reason of their richness, especially suitable for the purpose. The coloration of the collodion has to be very intense, so that every one of the extremely thin threads appears sufficiently dyed.

The mixture of the coloring matter with the collodion has to be effected before the latter is filtered, this being the easiest way of coloring the solution uniformly throughout,

so that the threads always show exactly the same color. However, with the use of colored solutions the contents of at least one cylinder have to be used all at once, and thus the quantity of silk of a determined color is quite limited.

For this reason the production of silk from colored solutions has been almost entirely abandoned, white silk only being prepared, which, after having passed through the processes previously described, is dyed like natural silk. Artificial silk prepared from nitro-cellulose possesses the property of readily fixing the coloring matter, and nearly all shades of color can be produced by simply immersing it in the dye solutions, the process being exactly the same as that employed in dyeing natural silk, and at present aniline colors are preferably used.

A comparative table of the properties of artificial silk prepared according to the various methods will be given later on, and hence those of Chardonnet silk need here only be briefly referred to. As regards lustre, it surpasses by far the finest qualities of natural silk, and when worked, either in an uncolored or colored state, into fabrics, it produces more beautiful effects than tissues of genuine silk. However, while the latter is distinguished by great strength and tenacity, artificial silk possesses these properties in a far less degree. By taking the elasticity of natural silk at 100, that of the best quality of Chardonnet silk is at the utmost 66, hence only about two-thirds. Fabrics made of artificial silk alone would not prove very durable, and hence in weaving them, pure silk or another fibre is generally used for the warp and artificial silk for the woof.

DU VIVIER'S ARTIFICIAL SILK.

This process for the preparation of a product closely resembling in appearance natural silk, was made known in 1889. It differs only in a few details from Chardonnet's method, nitro-cellulose being also used as the basis-material for its preparation.

The method of preparing this product known as *soie de France* is briefly as follows :

Cotton or in place of it, artificially-prepared cellulose is in the ordinary manner purified by treatment with alkalies —either soda or ammonia—and then converted into nitro-cellulose. However, instead of using a mixture of nitric and sulphuric acids, Du Vivier falls back upon the old method of nitration in which dry saltpetre and sulphuric acid are used as nitrating fluid, and effects the treatment of the cellulose at a comparatively high temperature—140° to 176° F.—till trinitro-cellulose is obtained.

In working with saltpetre and sulphuric acid, potassium sulphate is formed. This salt being distinguished by its comparatively slight solubility, it can only with surety be removed from the nitro-cellulose by subjecting the latter to a thorough treatment with water, and the consumption of wash water must necessarily be still larger than is the case in Chardonnet's process.

The solvent for the nitro-cellulose has to be considered as the main feature of Du Vivier's method. He uses for this purpose highly concentrated acetic acid (glacial acetic acid) in the proportion of 100 parts of it to 7 parts of nitro-cellulose. The nitro-cellulose obtained in this manner is mixed in varying proportions with a fine quality of glue (isinglass) and gutta-percha, and then worked into threads. The latter are conducted through various baths prepared from solutions of metallic salts—alumina salts and sublimate solutions being used—the object of which is very likely to transform the glue contained in the mass into an insoluble combination. The finished threads have finally to be subjected to denitration as, like other nitro cellulose silk, it would otherwise be highly inflammable.

As far as known, Du Vivier's process has not been successfully introduced in practice. Some samples of the silk submitted for examination are said to surpass the Chardonnet product in beauty of lustre.

Regarding the mechanical part of preparing the threads, nothing need to be said here, as, with the exception of slight modifications, it can only be carried on in a manner similar to that described more fully when speaking of Chardonnet's process.

LEHNER'S ARTIFICIAL SILK.

The third process for the manufacture of artificial silk from nitro-cellulose, which has thus far become known, is that of Lehner. It is now practically carried on on a large scale, and threatens to become a serious competitor of Chardonnet's system.

Lehner also starts with nitro-cellulose capable of complete solution, but all information regarding the preparation of this nitro-cellulose is wanting. According to the patent, dated 1890, wood spirit (methyl alcohol) is used as solvent for the nitro-cellulose, and to this solution, a solution of fibroin is added. The fibroin, *i. e.*, the fibrous portion of natural silk, is obtained from waste in silk spinning establishments, it being purified and dissolved in concentrated acetic acid.

According to a modification made public later on, in place of fibroin solution, solution of rubber prepared from drying oils, may be added to the nitro-cellulose solution. The solutions mixed in certain proportions—which, however, are not given—are pressed through spinners, and conducted through a vessel containing petroleum, chloroform, or oil of turpentine. The thread coagulates in these fluids so far as to acquire a thick, gelatinous condition, thus representing a very viscous mass. This state of the thread is utilized to make it still thinner by stretching, when it is wound on reels.

According to the present state of the manufacture of artificial silk, but two processes for its production from nitro-cellulose which can actually be carried on a large scale, are known, namely Chardonnet's and Lehner's. It

is scarcely to be expected that another process will be added to them, since Pauly's artificial silk and lustra-cellulose prepared from viscose, compete to such an extent with the products prepared from nitro-cellulose, that this competition will very likely end in the abandonment of the manufacture of artificial silk from nitro-cellulose.

DENITRATION OF ARTIFICIAL SILK.

The absolute necessity of denitrating artificial silk prepared from nitro-cellulose is one of the weakest points of the entire process, it being extremely difficult to effect denitration to the extent required without impairing the beauty of the product.

H. Richter has made exhaustive investigations regarding the denitration of artificial silk from nitro-cellulose, and, according to his statements, denitration as effected by his method, does not impair in any way the qualities of the silk as regards lustre, etc. The pith of Richter's method is the treatment of the silk with such metallic salts as have lower and higher degrees of oxidation, the solutions of the lower degree of oxidation being used with the addition of an acid. Among the metallic salts adapted for this purpose, the cuprous compounds are said to be most suitable, complete denitration being effected by cuprous chloride and cuprous oxychloride. Besides the cuprous compounds, there may be used, either by themselves or in a mixture of them: Ferrous, manganous, chromous, tungstous, stannous, mercurous salts, and the ferro-cyanide and metallic cyanide combinations.

For the purpose of accelerating the denitrating process, substances which cause the artificial silk to swell up may be added to the fluid and, in addition to alcohol and ether, mention is made of a long series of substances as being suitable for the purpose, for instance, oil of turpentine, glycerine, indifferent hydrocarbons and their derivatives, rubber solutions, and particularly isinglass. It is claimed that

such additions cause denitration to progress smoothly and completely, and that the full strength of the fibres is preserved. With the use of cuprous salts for denitration, such additions are said not to be required. In regard to the quantity of acid to be used, it is only necessary to take enough of it to convert the lower degree of oxidation into the higher one.

As a special advantage of his process, Richter mentions the possibility of recovering the nitrogen compounds, especially the nitric oxide, which are separated by denitration. However, according to our view of the matter, the recovery of the nitrogen compounds would actually pay only when denitration is effected with large quantities of artificial silk. For this purpose, air-tight vessels would have to be used for denitration, from which the nitric oxide evolved is constantly sucked off, and then oxidized by bringing it in contact with oxidizing bodies such as hydrogen peroxide or solution of potassium permanganate. The nitric oxide may also be directly conducted into sulphuric acid and, after adding an adequate quantity of nitric acid, this acid may again be used as denitrating fluid. The oxy-salts formed in denitration may also be reconverted into the lower degree of oxidation, so that the operation can be constantly carried on with a given quantity of the metallic salt.

If, for instance, cupric salts have been used, the fluid, after denitration, only contains cuprous salt. By adding to this fluid common salt and conducting sulphur dioxide through it, the cuprous salt is again reduced to cupric salt. Reduction is effected in a still more simple manner by placing copper plates in the acid fluid. In a similar manner the higher degrees of oxidation of other metals may by suitable reducing agents be reconverted into the lower ones, for instance, stannic chloride by ferrous chloride.

Some methods have also been devised with the object in view of preparing from the start a product which is not inflammable and, hence, does not require denitration. Such

a process has, for instance, been patented in England, by A. Peit, according to which 100 parts of nitro-cellulose, 7 parts of gum solution and 5 parts of stannous chloride dissolved in benzol are used. What is to be understood by gum solution is not entirely clear from the patent specification, and as gum solutions cannot be combined with benzol to a homogeneous fluid, it may be supposed that rubber is meant. It has thus far not transpired whether Peit's process has anywhere been introduced in practice.

From the present state of the industry it has to be acknowledged that artificial silk prepared from nitro-cellulose is distinguished by a beautiful appearance, as well as by relatively great tenacity and elasticity. The mechanical portion of manufacture has also been brought to such perfection as to allow of the production of artificial silk on the most extensive scale.

However, as previously mentioned, the process has one weak point, in that denitration is absolutely necessary, and by this operation the beauty of the product will remain unimpaired only when the greatest care is exercised. The particulars regarding the operations of denitration thus far made public are only partially satisfactory.

Particular attention has to be drawn to the fact that the production of artificial silk from nitro-cellulose has the decided drawback of the operation being by no means free from danger to the workmen. Notwithstanding all the precautionary measures taken in the factories, spontaneous ignition has frequently occurred, and in one case at least it was accompanied by explosive phenomena. That there is never absolute safety as regards spontaneous ignition is shown by the behavior of nitro-cellulose in drying. As mentioned in describing the manufacture of nitro-cellulose, the latter becomes electrical so readily that the passage over it of a warm current of air may lead to the formation of such a large quantity of electricity as to cause the formation of a spark. Even if the latter be never so small, it is of

sufficient power to ignite the nearest particles of nitro-cellulose, and the ignition of the entire mass must inevitably follow. Hence, in the production of textile threads from nitro-cellulose, special care must be taken that up to the time when the threads are subjected to denitration, they contain such a large content of water as is consistent with the operation, because spontaneous ignition of the nitro-cellulose can only under these conditions be positively prevented. In addition to this precautionary measure, attention must be paid to the health of the workmen by providing means for carrying off the vapors of ether and alcohol evolved during the coagulation of the threads. The precautionary measures which have to be adopted in this respect have been previously referred to.

X.

CELLULOSE THREADS. (CELLULOSE ARTIFICIAL SILK AND LUSTRA-CELLULOSE.)

Several methods, according to which it seems feasible to convert cellulose into a solution from which textile threads may be produced, are at present known, and some of them have been applied to the manufacture of textile threads on a large scale. As will be seen from the descriptions given below, these methods possess decided advantages over the process in which nitro-cellulose solution is used. These advantages are so great that from a purely economical standpoint, it may be safely predicted that these methods will more and more gain ground, and that cellulose-silk will finally be made so cheaply as to exclude the profitable production of nitro-cellulose silk. The main advantage of textile threads from cellulose is undoubtedly that they are no more inflammable than fabrics of any other kind of cellulose, for instance, cotton. Another advantage is that the manufacture itself is far more simple than can possibly be the case with nitro-cellulose. In addition, it may here be remarked that, as regards lustre and beauty, fabrics of cellulose threads compare favorably with nitro-cellulose silk.

While cellulose dissolves in a number of fluids, only one solvent, namely cuprammonium, need here be considered. This combination has for a long time been used by microscopists for distinguishing vegetable tissues. The object under the microscope is moistened with cuprammonium solution which causes the portions of tissue consisting of cellulose to disappear, they being dissolved in the fluid.

The residue remaining behind consists of other combinations.

The idea of utilizing the solubility of cellulose in cuprammonium for the preparation of textile fibres is of modern conception, and to Dr. Hermann Pauldy, of Gladbach, is due the merit of having invented a process by which such threads can be produced on a large scale.

DR. PAULY'S ARTIFICIAL SILK.

The preparation of textile threads (artificial silk) according to Dr. Pauly's method includes a series of operations, which, as far as the actual production of the thread is concerned, may be sub-divided as follows :

1. Preparation of pure cellulose.
2. Preparation of a solution of cellulose in cuprammonium of such concentration that, when pressed through apertures, a thread results which possesses sufficient tenacity to allow of its being stretched lengthwise.
3. Separation of the cellulose in the thread.
4. Washing, drying, throwing of the thin cellulose threads.

To these operations have to be added the preparation of the cuprammonium solution and the recovery of the copper from the fluids used, the endeavor being made to regain as far as possible the entire quantity of copper used in the operation so that the same quantity is in constant circulation in the factory.

PURIFICATION OF THE COTTON.

The cotton to be used has, previous to its solution in cuprammonium, to be subjected to a thorough cleansing process, this being effected in a manner similar to that previously described. Quite pure cotton is washed in a washing drum with soda solution, while for less pure material, dilute caustic soda solution is used.

The cotton treated with one of these fluids is whirled in

a centrifugal, thoroughly washed with water, then again whirled in the centrifugal, and finally completely dried. For the latter purpose artificial heat has to be employed, otherwise the cuprammonium solution would be too much diluted by the water contained in the cotton, the consequence of which would be loss of viscosity.

DISSOLVING THE COTTON IN CUPRAMMONIUM.

The cotton when perfectly dry is dissolved in cuprammonium, the preparation of which will be described later on. For 45 to 50 grammes (1.41 to 1.76 ozs.) of cotton, 1 liter (2.11 pints) of cuprammonium is used, this concentration being sufficient to yield a fluid capable of being spun.

According to statements made public, solution is to be effected in an apparatus closely resembling a montejus. However, since the latter apparatus consists of only a single vessel closed on all sides, in which the fluids are forced upwards through a rising pipe, it would not seem very well adapted to the purpose of dissolving the cotton, though it might answer for storing the solution till it is to be used.

For the purpose of dissolving the cotton as rapidly as possible in the cuprammonium, a mechanical contrivance of such a character is required that the cotton is kept in constant motion and that fresh portions of it are continually brought in contact with the solvent.

An apparatus resembling a hollander but constructed in accordance with the nature of the mass to be worked in it, would appear very suitable for the purpose of dissolving the cotton. The elliptical bottom of the trough of the hollander should be either of wood alone, or preferably, for the sake of durability, of wood lined inside with stout copper-sheet. The trough should be furnished with an air-tight lid to prevent decomposition of cuprammonium by the evaporation of ammonia. One of the compartments should be furnished with a grinding contrivance consisting of a corrugated bottom-plate and a corrugated cylinder revolving

at a short distance above the bottom-plate, and effecting the comminution of the mass passing through it. The bottom-plate, as well as the cylinder revolving above it, should be either of copper or another material not attacked by the fluid. Iron or steel is, in this case, entirely excluded, because the copper contained in the fluid would be separated from it in metallic form.

Solution is effected by bringing the weighed quantity of pure cotton into the hollander, closing the latter, and allowing cuprammonium solution to run in slowly, the mechanism which effects the revolution of the cylinder over the bottom-plate being at the same time set in motion. In the commencement of the operation only a small quantity of the solution should be run in, so that the cotton becomes first saturated with it before the entire quantity is introduced. By the continued tearing between the bottom-plate and cylinder, the particles of cotton are uniformly distributed throughout the fluid, solution being under these conditions effected in the shortest time possible. In practice, 10 hours are generally calculated on as being required for the preparation of the solution, but with the use of an apparatus similar to the one above described, it may be effected in a much shorter time.

The progress of solution is judged by the appearance of samples taken from time to time and allowed to stand quietly for 10 minutes in a tall, covered glass cylinder. If solution has been properly effected, the fluid is perfectly clear and of a uniformly blue color without cloudiness. If the lower portions of the fluid show a different color, or a precipitate is noticed, it is indicative of a considerable portion of the cotton remaining in an undissolved, or only in a very much swollen, state. The manipulation in the hollander has then to be continued till the sample shows no longer a want of uniformity.

Although the fluid appears to the eye perfectly uniform, it may nevertheless contain considerable quantities of cot-

ton fibres only very much swollen without being actually dissolved. Such fibres would make the solution unsuitable for spinning, a viscous fluid absolutely free from solid bodies being only adapted for that purpose. Hence, the solution must by all means be filtered, filtration being, in this case, also effected in an entirely closed apparatus in which the fluid stands under such a high air-pressure as to be forced through the close pores of the filtering body, a substance entirely indifferent towards the action of cuprammonium being used for that purpose. Cotton is unsuitable for a filtering material, since by the action of the cuprammonium it would in a short time swell up so much that no fluid could be forced through it even by the strongest pressure. Plates of compressed asbestus-felt with pores sufficiently close to retain the solid bodies suspended in the fluid are very suitable for filtering purposes. The residue remaining upon the filter consists chiefly of the more solid portions of the cuticles of the cotton fibres and remnants of plasma.

The filter is fitted up in a similar manner to that described under Chardonnet silk. In a boiler-plate cylinder stands a vessel of sheet copper which serves for the reception of the fluid to be filtered. Upon the bottom of this vessel lies the asbestus plate enclosed in two plates of copper-wire cloth. Below the filter-plate the copper cylinder terminates in a truncated cone and is connected with a copper vessel which serves for the reception of the filtered solution.

The pressure upon the fluid in the vessel is produced by compressed air, and should be of sufficient force to effect filtration with suitable rapidity. Solutions of cotton in cuprammonium being by far less viscous than nitro-cellulose solutions, less pressure is required, one or a few atmospheres being sufficient.

If the pipe leading from the filter be allowed to enter a montejus, the solution collects in the latter and may be raised by air-pressure through the rising pipe of the montejus into the vessel in which the spinning apparatus is placed.

SPINNING THE SOLUTION.

The spinning vessels closely resemble those used in Chardonnet's system. They consist of closed sheet-steel cylinders lined with copper, in which the fluid can be placed under increased pressure.

The contrivance in which the formation of threads is effected is, however, of peculiar construction. The solution of cotton in cuprammonium is also distributed in a horizontal pipe to which the spinners are secured, the latter being, however, of a characteristic shape. They are placed obliquely and bent slightly upwards, so that the fluid emerging from them ascends upwards in an oblique direction. The apertures of the spinners lie beneath the level of a fluid consisting of water containing 15 per cent. of sulphuric acid.

The spinners through which the solution passes into the dilute sulphuric acid are in construction similar to those of the Chardonnet system, but as will be directly explained, threads of a considerably smaller diameter than that of their apertures can be obtained from them.

The moment the cellulose solution passes into the sulphuric acid, it is decomposed, a solution of cupric sulphate (blue vitriol) and ammonium sulphate being formed. The solvent being decomposed, the cellulose must separate in a solid state, this separation taking place in the form of a soft cylinder of a gelatinous nature which possesses a high degree of extensibility. This behavior is utilized for making the thread still thinner by stretching.

The threads—usually 18—as they come from the lead trough containing the sulphuric acid are run through a glass gatherer or collector, so that the thread thus formed is actually composed of 18 separate threads. Back of this gatherer, revolves with suitable velocity a glass roll on which the thread is wound under a certain tension, thus being stretched. The glass roll while revolving is also with

the requisite velocity moved sideways so that the thread is wound up in windings one alongside the other.

The cellulose, by reason of its larger content of water being much too soft to stand rinsing off before being brought upon the glass roll, washing has to be effected upon the latter itself. This is best done by placing a number of such glass rolls in a mechanical contrivance, which causes them to revolve slowly in a trough constantly supplied with fresh water, in which they remain till the last traces of sulphuric acid have been removed.

When washing is finished, the cellulose threads are dried at a higher temperature by bringing the glass rolls into a drying room. By the slight contraction the threads undergo in drying, their fineness and lustre are still further enhanced.

The further manipulation by mechanical means of the cellulose threads prepared in the above described manner, is effected in exactly the same way as in silk-spinning works. The thread is wound from the glass rolls on spools, and thrown. The finished threads suitable for spinning may be dyed in the skein. They are mordanted in various ways according to the coloring matter to be used, and left in the dye bath till the desired tone of color is obtained.

As compared with the product prepared from nitro-cellulose, the properties of the artificial silk, or rather pure cellulose, prove very satisfactory. As regards tenacity and elasticity, it is at least equal to Chardonnet silk, and possesses the rustle characteristic of genuine silk. A special advantage of Pauly's silk is found in the fact that its production is free from all danger, no poisonous vapors being evolved, and the use of a substance, like nitro-cellulose, which is dangerous to handle, is excluded. Finally, Pauly's silk does not require denitration, which is absolutely necessary with the product from nitro-cellulose, and this evidently constitutes the most valuable feature of the process. With reference to the point of expense, it will be seen at the first glance on comparing Pauly's method with the nitro-

cellulose process, that the cost of production by the latter must be considerably greater, the cellulose having first to be converted into nitro-cellulose, and then as far as possible again reduced by denitration to cellulose. From the advantages enumerated here, both as regards manufacture and properties, it would seem that Pauly's method will in the course of time drive nitro-cellulose silk out of the field.

E. BRONNERT'S PROCESS.

This method for the preparation of textile threads from solution of cellulose in cuprammonium differs essentially from Pauly's, the cellulose being first converted into soda-cellulose which is effected with caustic soda, and then triturated with cupric sulphate (blue vitriol). A double conversion takes place thereby, sodium sulphate being formed and a loose combination of cupric hydrate and cellulose. By treating this combination with ammonia, a solution possessing a considerable degree of viscosity, which it retains at a higher temperature, is obtained, and consequently it yields good threads capable of being spun.

In carrying out the process, it is necessary to use the separate substances according to molecular weights. For 162 parts by weight (1 molecule) of dry cellulose in a finely divided state, 80 parts by weight of pure sodium hydrate dissolved in 500 parts by weight of water are used, the cellulose being intimately mixed with the fluid. In the course of an hour, 249 parts (1 molecule) of finely powdered crystallized cupric sulphate are added to the mass and the whole is intimately mixed, a rise in the temperature being carefully avoided. A uniform mass of a pale blue color is formed. Concentrated ammonia is then poured over the mass, in such quantity that for every molecule of cupro-hydrocellulose, 16 to 20 molecules of ammonia are used. Solution takes place immediately, and the greater portion of the sodium sulphate remains behind undissolved.

The further working of the solution of cellulose in cuprammonium prepared according to this method is exactly the same as in Pauly's process previously described.

PREPARATION OF CUPRAMMONIUM.

Besides purified cotton, cuprammonium is the most important product used in the manufacture of artificial silk according to Pauly's method, and its preparation constitutes an essential part of the entire manufacture. Commercial cupric sulphate or blue vitriol is, as a rule, used as the initial material, but in buying it, it must be taken into consideration that, as found in commerce, it is frequently very impure and contains a considerable quantity of ferric sulphate. A product almost chemically pure is only available for our purpose.

For the preparation of cuprammonium, cupric sulphate is dissolved in a sufficient quantity of water to form a saturated solution. As well water always contains a certain quantity of carbonates, which cause a separation of cupric carbonate, the solution is not clear, but more or less of a milky turbidity. This turbidity may, however, be readily removed by carefully adding to the fluid a small quantity of sulphuric acid and stirring thoroughly, the separated cupric carbonate being thereby redissolved, and the clear fluid then contains only cupric sulphate in solution.

For the sake of precaution, the solution is filtered into another vessel, and after bringing it into brisk motion by means of a spatula, ammonia is added, a voluminous pale blue precipitate consisting of cupric hydroxide being formed. After each addition of ammonia, the fluid is thoroughly stirred and a small sample, previously filtered through paper, tested. If, on adding to the fluid in the test-tube a drop of ammonia, a precipitate of cupric hydroxide is formed, it is proof of all the copper in the fluid not having been separated; and more ammonia has to be added.

When a fresh sample remains colorless, and after the

addition of a drop of ammonia, no noticeable changes are observed in it, it is proof of all the copper having been separated in the form of cupric hydroxide. Care must be taken not to add a larger quantity of ammonia than absolutely necessary for the precipitation of the cupric hydroxide, because by an excess of ammonia the cupric hydroxide just separated would be redissolved, and the fluid again acquire a deep, dark-blue coloration.

When precipitation of the cupric hydroxide is complete, the contents of the vessel are allowed to stand quietly till the precipitate has settled to the bottom. The colorless supernatant fluid consisting of solution of ammonium sulphate in water may be utilized as a fertilizer.

By opening tap-holes placed at different heights in the wall of the precipitating tank, the solution of ammonium sulphate is drawn off as far as possible. Clear water is then poured over the precipitate and, after distributing the latter in the water by stirring, it is again allowed to settle. The supernatant clear fluid is again drawn off, and this washing of the precipitate is several times repeated till it may be supposed that all the ammonium sulphate has been removed. The pasty precipitate is then brought upon large cloths suspended by the corners, and allowed to remain upon them till no more water drains off; a certain quantity of water is also removed by squeezing. For the purpose of determining exactly the quantity of water still contained in the mass, a weighed sample is dried at a moderate heat and then again weighed; the loss in weight gives the quantity of water still contained in the mass and from it, is calculated the content of cupric hydroxide. Drying the sample used for this test should be effected at a temperature not exceeding 176° F., the cupric hydroxide being readily decomposed by heating, to black cupric oxide and water.

The cupric hydroxide is now brought into the apparatus in which it is to be converted into cuprammonium. This apparatus consists of a closed vat provided with a stirrer

furnished with several paddles. While the stirrer is slowly revolving, the weighed quantity of cupric hydroxide is brought into the vat, and the ammonia is then allowed to run in. The cupric hydroxide dissolves readily to a clear, dark-blue fluid.

When the stirrer has for some time been kept in motion, a small sample of the fluid is taken from the vat and allowed to stand quietly in a test-tube. If a precipitate is formed it is indicative of the total quantity of cupric hydroxide not having been dissolved, and more ammonia has to be added. Although an excess of ammonia does not hurt, it is a useless waste of material. The solution of cuprammonium is made of such a concentration that 1 liter (2.11 pints) contains between 10 and 15 grammes (0.35 to 0.52 ozs.) of copper, the desired concentration being determined by means of an aerometer. Solutions with this content of copper are capable of dissolving between 45 and 50 grammes (1.41 to 1.76 ozs.) of cotton in 1 liter (2.11 pints) and the resulting solutions possess sufficient viscosity to yield, when decomposed by sulphuric acid, a thread of such tenacity as to allow of its being wound on the previously-mentioned glass roll.

According to the process of E. Bronnert, M. Fremery and J. Urban, the preparation of solution of cuprammonium as solvent for cellulose is effected by filling a tall cylinder with copper-turnings and ammonia, and allowing cooled compressed air to ascend for ten hours in the cylinder. During this time the temperature of the fluid should not exceed 41° F., and for this reason the cylinder is furnished with a jacket in which cooled common-salt solution constantly circulates. At a higher temperature the dissolved cupric hydroxide would rapidly separate, and the content of copper in the fluid would not amount to over 2 to 2.5 per cent. The solution thus obtained must also be kept at the same low temperature during the time required for the solution of the cellulose.

The solubility of cellulose is claimed to be considerably

facilitated by previously subjecting it to thorough bleaching. For this purpose it is for 18 hours placed in a 15 per cent. chloride of lime solution, then washed and immediately brought into the cuprammonium. Cellulose thus treated dissolves to within 10 per cent.

The mode of bleaching mentioned above is of great importance as regards the quality of the solution, cellulose more vigorously bleached yielding a solution which is not sufficiently gelatinous for the purpose of producing serviceable textile threads.

Cellulose also very readily soluble in cuprammonium is said to be obtained by treating it in the same manner as for the preparation of vegetable parchment: Immersion for a short time in quite concentrated sulphuric acid, and then washing with water for the complete removal of the acid. For the production of threads from a solution of such cellulose in cuprammonium, the solution emerging from the spinners is simply precipitated with an acid, and the thread can be immediately wound on a roll, and dried at 104° F.

RECOVERY OF THE COPPER.

By the decomposition of the cuprammonium in the dilute sulphuric acid when the solution emerges from the spinners, the entire quantity of copper contained in the fluid remains behind in the sulphuric acid, the same being the case with the ammonia. Hence, in addition to cupric sulphate the fluid contains ammonium sulphate, and the copper has to be recovered. This may be effected in various ways, and depends on whether or not the ammonium sulphate dissolved in the fluid is to be utilized.

The simplest plan for the recovery of the copper is to treat the fluid with iron when it has been so far exhausted that it contains only a very small quantity of free sulphuric acid. By moving to and fro sheets of iron suspended in the fluid, copper in the form of a loose powder is separated, a corresponding quantity of iron being dissolved. The fluid

remaining behind then contains, in addition to ammonium sulphate, ferrous sulphate (green vitriol) in solution. The separated copper only requires washing with water, and by treatment at a moderate heat with hydrochloric acid can be redissolved. The solution which then contains cupric chloride may be immediately used for the preparation of cupric hydroxide.

However, another plan may be adopted by which the ammonium sulphate may also be recovered and utilized by itself. The dilute sulphuric acid in which the decomposition of the cellulose solution is effected, is used until it contains but a very small quantity of sulphuric acid in a free state, when it is replaced by fresh acid. The fluid is then mixed with ammonia, the free sulphuric acid present being thereby converted into ammonium sulphate. By the addition of still more ammonia the cupric hydroxide begins to separate, and by adding the correct quantity of ammonia all the copper present may be separated. The precipitated cupric hydroxide is again used for the preparation of solution in ammonia, and theoretically, unlimited quantities of cellulose can be brought into solution with one and the same quantity of copper. The fluid freed from copper now contains ammonium sulphate in solution, which may be utilized by itself, the simplest plan being to employ it as a fertilizer, as the crystallization of such a comparatively small quantity of the salt would not be worth the trouble.

After Chardonnet's process for the production of textile threads from nitro-cellulose solution became known, other patents were taken out which, however, are essentially only modifications, the same having also been the case with Pauly's method, but the principle remains intact. In all the new processes solutions of cellulose in cuprammonium are worked, the innovations consisting only in the subsequent treatment of the thread obtained, which by this

treatment, it is claimed, acquires greater lustre, fineness and tenacity.

ARTIFICIAL SILK ACCORDING TO M. FREMERY AND J. URBAN.

The process patented by M. Fremery and J. Urban is said to yield threads of greater lustre and tenacity than those produced by Pauly's method. All the operations by this process up to the production of threads fit to be spun may be omitted, as they differ in nothing from Pauly's, the modification commencing only with the treatment of the thread when it emerges from the acid fluid. Without endeavoring to make them thinner by stretching, the threads while in a wet state are tightly wound on cylinders and allowed to dry upon them. The cylinders have quite a large diameter, so as to allow of a considerable quantity of thread being wound on them, and also of attaining greater tension during drying.

The thread thus produced forms a soft, gelatinous mass very rich in water. By gradually yielding water to the air, its diameter, as well as its length, is decreased, but being tightly wound on the cylinder quite a considerable longitudinal strain ensues, whereby it gains in fineness and smoothness. However, the thread is dried in the air only up to a certain degree, when the cylinder is brought into a room heated to 104° F., in which it remains until the thread is perfectly dry and can be wound on spools.

Drying the thread in the above-mentioned manner—first up to a certain degree at the ordinary temperature, and then with the use of a higher temperature—is of great importance. If on coming from the spinning apparatus it were immediately exposed to the higher temperature it would, without tightening, dry to a brittle, lustreless product of porcelain-like appearance.

According to observations of the patentees two phases may be distinctly observed in the drying process. In the beginning a considerable quantity of water evaporates

in a comparatively short time. Evaporation then takes place very slowly, so that it may be supposed that a certain quantity of the water is chemically combined with the cellulose. This water may be rapidly brought to evaporation with the use of a higher temperature, but in this case the thread becomes brownish and loses lustre and tenacity.

This drawback may be avoided by submerging the cylinder for a short time in water heated to between 158° and 212° F., or by allowing a current of steam to act upon it. This treatment is claimed to separate the chemically fixed water from the combination, and the process of drying is then effected in one-quarter the time which would otherwise be required.

In addition to this innovation, which actually relates only to the mechanical manipulation of the cellulose thread, E. Bronnert, M. Fremery and J. Urban have introduced another modification which refers to the production of the thread itself. Instead of using for the decomposition of the cellulose solution in cuprammonium, a fluid which contains only 15 per cent. sulphuric acid, as is the case in Pauly's method, they employ a fluid which contains between 30 and 65 per cent. sulphuric acid, a fluid with 50 per cent. sulphuric acid yielding, according to their statements, the best results.

The thread passing from the spinner into such a fluid becomes immediately so firm and tenacious that the very disagreeable breaking of it does not happen, and consequently it can be allowed to emerge with great rapidity from the spinners and wound on the cylinder. The thread obtained in this manner is then further treated in the usual way, and yields a product which, as regards firmness, tenacity and lustre, answers all requirements.

The effect of concentrated acid may be explained as follows: The solution of cellulose in cuprammonium is decomposed the moment it passes into the sulphuric acid, hydro-cellulose being separated. However, by the great

affinity of concentrated sulphuric acid for water, this combination is immediately again decomposed and pure cellulose formed, which contracts quite considerably, thus forming a much firmer and more tenacious thread than is otherwise the case. It may, however, also be possible that by the action of the sulphuric acid, a thin layer of the cellulose is dissolved upon the surface of the thread and again separated, when the latter passes into less concentrated acid, the thread becoming thereby, so to say, varnished.

If the chemical process actually runs its course in the above-described manner, it has a certain resemblance to that which takes place in the manufacture of vegetable parchment. By the immersion of the paper in concentrated acid, a contraction of the felted cellulose fibres is, on the one hand, effected, while on the other, a solution of the uppermost layer of cellulose immediately takes place. From this solution, when brought in contact with water, a substance is separated which, like a varnish, lies upon the surface of the paper, firmly cements together the individual fibres in the interior, and thus effects the great strength of vegetable parchment.

ARTIFICIAL HORSE-HAIR.

When thread resembling genuine silk in appearance, as closely as possible, is to be produced from cellulose solution, a spinner with an aperture of a very slight diameter is used and the diameter of the thread, while the latter is still soft, is sought to be further reduced by stretching. Chardonnet, as previously mentioned, uses a spinner with an aperture only $\frac{8}{100}$ millimeter in diameter, and by stretching the thread, while soft, its diameter may be considerably reduced. By the use of a spinner with a larger aperture, thread of a larger diameter may of course be obtained, though a certain limit should not be exceeded. When the thread exceeds a certain thickness, the decomposition of the combination and the separation of pure cellulose do not

take place with such completeness as is required in order to obtain a uniform product.

For the production of uniform threads of larger diameter, another method must therefore be adopted which is essentially as follows: Spinners with apertures so large as is consistent with the preparation of a uniform thread are used. A number of such spinners are so placed that the threads emerging from them touch each other, just after they have been formed, while they are still beneath the level of the fluid. In this state—so to say, at the moment of formation—the threads unite, and there is no difficulty whatever, in thus obtaining threads, which as regards their diameter, are equal to horse-hair, and even surpass it.

The threads thus obtained may be dyed any color desired, and are claimed to be available for all purposes for which horse-hair is at present used. In the textile industry, such threads might be utilized for the preparation of the warp for especially strong fabrics capable of great resistance, for instance, sail cloth. These threads are claimed to be especially adapted for filaments for incandescent electric lamps, and may also be advantageously used for making the incandescent body of gas light.

XI.

TEXTILE THREADS FROM VISCOSE (THREADS FROM LUSTRA-CELLULOSE.)

Viscose solution when exposed to the air coagulates in a short time to a solid mass consisting of cellulose, and to obtain the latter in a perfectly pure state, it is only necessary to remove the alkali present by treatment with water. If viscose be allowed to emerge from tubes with a cylindrical cross-section, threads suitable for textile fabrics are obtained.

By reason of the great simplicity of the process of obtaining pure cellulose from viscose, much attention is very likely to be paid to the production of textile threads from this material. As shown by experiments on a small scale, such threads possess exactly the same properties as artificial silk prepared according to Pauly's method—because threads prepared from viscose consist of the same body as Pauly's silk, namely, cellulose, the only difference being in the manner of producing them. As shown by the experiments above-mentioned, thread prepared from viscose possesses a surprisingly high degree of lustre, and the term lustra-cellulose may properly be applied to it.

Experiments made on a somewhat larger scale also yielded very favorable results, the thread exhibiting a magnificent silky lustre, and, therefore, viscose also would seem to have a great future for the manufacture of textile threads and fabrics. The cost of producing the threads will very likely not be any larger than in working according to Pauly's method, and is certainly far less than that of artificial silk made by Chardonnet's process.

Threads made from viscose are distinguished by an exceedingly small diameter, being in this respect at least equal to the finest quality of natural silk. In addition they possess great lustre and considerable strength, yielding, when woven, fabrics of great beauty which, without any further finishing, may be called glossy stuffs in the actual sense of the word. The viscose intended for the preparation of threads may be colored throughout the entire mass by simply adding coloring matter and thus, in a single operation, textile, and at the same time dyed, threads may be produced, which, after being thrown in the usual manner, may be woven into fabrics. With the use of viscose not dyed, pure white fabrics requiring no special bleaching or finishing are obtained.

Since for the production of textile threads, materials are used which in themselves possess but little value, such as old purified cotton, or waste paper, or finally bleached cellulose from wood, the raw material is considerably cheaper than that used for the production of artificial silk from nitro-cellulose, and fabrics of lustra-cellulose are consequently cheaper than those of artificial silk, but withal of equal beauty. Together with Pauly's artificial silk, they will be able to compete triumphantly with artificial silk from nitro-cellulose.

While artificial silk from nitro-cellulose is extraordinarily inflammable, and fabrics manufactured from it before being brought into commerce have to be subjected to denitration, tissues of lustra-cellulose are no more inflammable than ordinary linen or cotton fabrics, because they consist of pure cellulose.

The factories engaged in the production of fine threads from viscose keep the apparatus used for the purpose a profound secret, but the construction of such an apparatus presents no difficulties, many portions of it corresponding with that generally used for the preparation of artificial silk threads. It is, however, of the utmost importance that

the viscose should be used in the form of a solution absolutely free from solid bodies. Many viscose solutions appearing perfectly clear to the eye, may, nevertheless, contain entirely unchanged fibres of cellulose or nitro-cellulose, which have escaped the action of the carbon disulphide, they being invisible, because they possess quite the same power of refracting light as viscose solution itself. If such viscose were to be forced through the spinning apparatus, one after the other of the narrow apertures would soon be found to yield no thread whatever, and the apparatus could not be put in activity again even with the use of the highest pressure.

In working on a small scale, the preparation of a perfectly clear viscose solution presents no difficulties whatever, but solution does not progress quite so smoothly when operating on a larger scale, the viscose on being brought in contact with water swelling up very rapidly, and the swelled-up mass preventing the access of water to the interior portions. Hence to effect solution in a short time a mechanical contrivance has to be used by means of which the viscose is reduced and the formation of tough lumps prevented. A hollander is best suited for this purpose, as the thorough mixing of the solid mass with water can be effected by it in the most complete and rapid manner.

The trough of the hollander is first filled with the quantity of water to be used for dissolving a fixed quantity of viscose, and the mechanism having been set in motion, the viscose to be dissolved is introduced in small portions. The whole is then worked till a uniform viscous mass is formed in which no dark spots or streaks can be noticed with the naked eye.

However, the presence of undissolved particles can to a certainty be only prevented by filtering the finished viscose solution before introducing it into the spinning apparatus. Filtration of a fluid of such viscous nature as viscose causes considerable difficulties which may, however, be overcome

by the use of an apparatus especially constructed for the purpose. As filtering material, it is best to use porous plates of cellulose. These plates are placed upon a metal plate perforated like a sieve, which forms the bottom of a solidly constructed cylinder. The latter is furnished with a lid fitting air-tight, and by means of a pipe is connected with a condensing air-pump. The cylinder having been filled with the viscose to be filtered, the lid is placed in position and the air-pump set to work, the pressure upon the fluid being only gradually increased to prevent the filter-plate from being torn asunder. When the pressure has attained a certain height, the viscose commences to trickle through the filter, and it is only necessary to keep up the same pressure in order to secure a uniform flow of the fluid. When the charge in the filter is almost exhausted, fresh viscose is introduced through a pipe on the side of the cylinder, the operation being thus continued so long as the filter remains effective. When, notwithstanding increased pressure, filtration is observed to become more and more sluggish, it is indicative of the pores of the filter being much obstructed, and the useless plate has to be replaced by a fresh one. For the purpose of dislodging the last remnants of viscose contained in the pores of the filter-plate, pure water is introduced into the cylinder until nothing but water runs off.

This last remnant of viscose, which is quite dilute, is used in place of pure water for the preparation of fresh quantities of solution, and the cellulose plate which has become useless for filtration, is employed as raw material for the preparation of nitro-cellulose, nothing being thus wasted.

It is advisable to make provision for the direct passage of the clear, filtered viscose from the filter into the reservoir of the spinning apparatus, to prevent it from being changed by contact with the air.

The spinning apparatus consists in its main features of a

thick-walled metal vessel which can be closed air-tight, and can be connected with an air-compressing pump. In the bottom of this vessel sits the so-called spinning-plate, by means of which the formation of extremely thin jets of fluid is effected. In this spinning-plate are fixed a larger number of extremely narrow glass tubes conically enlarged above. The reservoir having been filled with the clear viscose solution, the air-compressing pump is set in motion, and the pressure increased to such an extent that the fluid is with a certain velocity forced from the narrow apertures.

The same pressure must be maintained throughout the entire spinning operation, because only in this way can jets of fluid be made to emerge evenly from the spinning apertures, and this is of the greatest importance for the uniformity of the threads.

By allowing the threads emerging from the spinning apertures to hang down free, they stretch to a considerable extent by reason of the viscous nature of the viscose. The resulting threads are of a still smaller diameter than the original ones, and they break only by their own weight after having attained a certain length. It being desirable to produce threads of as small a diameter as possible, the length to which they may hang down free without danger of breaking has to be determined by experiments. However, provision has then to be made for hardening them as rapidly as possible so that they may be reeled up.

While viscose coagulates by itself in the air, too much time would in the case in question be required for the purpose, and it must therefore be sought to convert it in as short a time as possible into a solid body—viscoid. The transformation of viscose into viscoid is the more quickly effected the higher the temperature to which it is exposed, and the viscose threads after having been stretched to a certain length must be further treated according to this principle.

This may be accomplished by the following arrangement:

The reservoir containing the viscose to be spun is placed at a higher level, and the threads emerging from the spinning plate sink down free in a shaft-like space. On the bottom of this space, the coagulated threads are drawn through glass eyes and conducted to the reels on which they are wound. The latter contrivances closely resemble those used in silk-spinning establishments for reeling silk from the cocoons. For the purpose of converting the fluid viscose thread into the solid viscoid thread, a current of hot air ascends in the shaft through which the threads sink down. By this hot current of air the mass is solidified and the greater portion of the water at the same time evaporated. The temperature and velocity of the current of air ascending in the shaft have to be accurately regulated and must be adapted to the rapidity with which the viscose is forced from the spinning apertures. The current of air must of course be so hot that the threads on reaching the lower end of the shaft are sufficiently firm and dry to allow of being reeled up. On the other hand, it must in ascending have already yielded so much heat, that the viscose emerging from the spinning apertures is not immediately coagulated, but retains sufficient viscosity to allow of the thread stretching to a certain extent in sinking down before reaching the layer of air in which it is entirely coagulated.

To bring about the co-operation of all the conditions by means of which threads of the proper quality can only be obtained, the same conditions must be adhered to in every particular. Thus it is by no means immaterial whether there is a difference of a few degrees in the temperature of the viscose in the reservoir, its consistency—greater or less degree of viscosity—being influenced thereby, as well as the time the thread requires for coagulation.

Efforts must, therefore, always be made to use viscose solution of the same temperature, and the apparatus furnishing the hot current of air should be so arranged that the temperature of the heated air can be exactly regulated,

this being accomplished without difficulty with the use of the so-called rib-heaters. The heater is enclosed in a box through which air is constantly forced by a small ventilator. By keeping the latter running uniformly and maintaining constantly the same expansion of steam, the air is heated in such a uniform manner that the temperature shows but exceedingly slight variations. If necessary, even the latter may be overcome by furnishing the box with a register by means of which the strength of the current of air may at will be increased or decreased, and the temperature in the shaft can thus be almost instantly raised or lowered.

The viscose threads wound on the reels are of such a small diameter that they cannot be worked by themselves. A larger number of them—how many depends on the fineness of the fabric to be made—are therefore taken together, and converted by mechanical means into skeins which can be woven, being further worked exactly as any other yarn.

PREPARATION OF TEXTILE THREADS FROM VISCOSE, ACCORDING TO STEARN.

According to Ch. H. Stearn's patented process, textile threads, as well as thin plates of viscoid, may be directly prepared by a simple method from viscose solution. The threads emerging from the spinning apparatus are immediately allowed to drop into solution of ammonium chloride (sal ammoniac) in which they at once coagulate and can be directly reeled up or thrown. By fitting the bottom of the vessel containing the viscose solution, with a narrow slit, in place of the narrow apertures which furnish cylindrical threads, the viscose solution is obtained in the form of a thin, broad band, which also solidifies immediately in the ammonium chloride solution. The thin plates thus obtained may be used for writing and printing, as well as for photographic purposes, they being especially suitable for the preparation of the long, narrow strips which serve for taking pictures for the cinematograph.

The cellulose threads prepared according to one or the other process have to be carefully washed, by being repeatedly brought in contact with fresh quantities of water. To be quite sure of all the alkali having been entirely removed, the threads are finally passed through pure, highly diluted acetic acid, and then dried in the air. The acetic acid which is not fixed evaporates thereby, and the threads then cannot contain any free alkali.

MILLAR'S ARTIFICIAL SILK (GELATINE SILK).

While in all the previously-described methods for the preparation of textile threads either nitro-cellulose or cellulose solutions form the basis-material, in Millar's process, as well as in a very similar one, published by Hummel, glue is used as the initial raw material. By reason of the great viscosity of glue solution it may be made into threads, and the glue contained in them can by suitable treatment be converted into an insoluble combination.

The textile threads thus produced have, however, not stood the test as compared with other artificial threads, and we may here confine ourselves to giving merely the outlines of the mode of manufacturing them.

According to Millar's process, 2 lbs. of glue of finest quality (gelatine) are broken up in small pieces and allowed for one hour to stand quietly together with 4 lbs. of cold water. The mass is then for two hours heated to 120.2° F., the result being a very thick solution in water which, when forced through narrow tubes, can be drawn into threads. The latter are conducted into a room filled with vapors of formaldehyde whereby the glue is rendered insoluble.

A modification of Millar's process, consists in adding to the glue solution a quantity of potassium dichromate equal to about 2 per cent. of the weight of glue used. The threads spun from the solution are exposed to the light whereby the glue is also converted into a combination insoluble in water.

While the threads obtained by either one of these processes, present quite a nice appearance, they do not possess sufficient flexibility and elasticity to be utilized for tissues. If a thread be once or twice bent, and then placed under the microscope, the bent places will be seen full of cracks, and by repeated bending the thread would break. A further disadvantage is that the threads swell very much in moist air.

By drawing gelatine threads after they have acquired a certain degree of solidity through solution of an aluminium salt, or tannin solution, their brittleness, as well as their tendency to swell up in moist air, is somewhat reduced, but the resulting product cannot bear comparison, as regards beauty and strength, with cellulose threads, and there is very likely no prospect of the production of gelatine threads which might be available for practical purposes.

GENERAL PROPERTIES OF TEXTILE THREADS PRODUCED BY ARTIFICIAL MEANS.

The textile threads produced by one or the other of the processes previously described, possess properties which in many respects differ essentially from those of genuine silk or of cellulose derived from plants, and, in dyeing as well as in weaving, they have to be differently treated.

Threads from nitro-cellulose, as well as from pure cellulose, possess much greater lustre than natural silk, and, in addition to this high lustre, are stiffer and more elastic, these properties being of great advantage in working them.

However, on the other hand, the manipulation of artificial silk is rendered very difficult by the fact, that, when brought in contact with water, the threads lose the greater portion of their tenacity, the latter, as shown by direct measurements, being reduced to $\frac{1}{6}$ and even to $\frac{1}{10}$ of the dry thread. The cause of this phenomenon is that the threads, on coming in contact with water, swell up very much, whereby the coherence of the separate particles is to a great extent broken up.

In dyeing threads of artificial silk, the above-mentioned facts have to be taken into consideration, and moderately warm dye-baths of a temperature not exceeding 140° F., should only be used. Great care must also be exercised in handling the skeins in the dye-bath to avoid breaking off a large portion of the threads. By reason of the threads swelling very much, they take the dye more rapidly than is the case with natural silk, and for delicate shades very dilute dye solutions have to be used, there being otherwise danger of over-dyeing.

When dyeing is finished, the skeins or fabrics must by no means be wrung out as may be done with natural textile fabrics, but must be freed from adhering dye-fluid by whirling in a centrifugal, further washing with water being also effected with the latter apparatus.

As regards the further properties of artificial textile threads, the microscope furnishes an excellent means for their examination, and with its assistance genuine silk can immediately be distinguished from the artificial material by the form of the latter, which in itself proves it to be an artificial product. While natural silk always appears as a smooth cylinder of uniform thickness with only a few cross stripes, the artificial thread never possesses such uniformity, being considerably thicker in some places than in others. It is, as a rule, not perfectly round, but more or less flattened, this being especially the case with Chardonnet silk, while Pauly's is much more uniform, its shape approaching more closely that of a cylinder.

The difference between natural and artificial silks becomes especially noticeable under the microscope on moistening the sample with water. While natural silk does not swell up to a noticeable extent by remaining even for a long time in contact with water, the artificial product immediately commences to swell up and acquires a width $\frac{1}{4}$ to $\frac{1}{3}$ greater than when dry.

The compilation given below is based upon micrometrical

measurements, and shows the diameters of various kinds of natural silk in a swollen state. To obtain the diameters of the threads in a dry state, deduct $\frac{1}{4}$ to $\frac{1}{3}$ from the figures given :

	Mean.	Maximum.
	μ	μ
Chardonnet silk	45 to 60	100
Fismes silk	40 to 80	120
Lehner silk	60 to 90	135
Pauly silk	40 to 50	75
Gelatine silk	60 to 80	85
Genuine silk	9 to 15	20

In the optical way, artificial silk, with the exception of threads prepared from gelatine, can also be immediately recognized by its double refraction of light. Genuine silk, to be sure, possesses the same power of refracting light but, with some practice, the difference between it and the artificial product can be readily discovered. By examining in the polarizing instrument a thread of genuine silk in such a way as to observe different portions of it, the same color phenomena will always appear. However, in consequence of its irregularity, such is not the case with artificial silk, the thicker places showing entirely different colors from the thin ones. On the places where the narrow side of the flattened thread is before the eye, the color, as a rule, is green or blue.

The richest color phenomena are observed in Lehner's silk, the separate threads showing colored longitudinal stripes which are yellow, red, green, or steel-blue, a proof of great variations in their dimensions.

The tenacity of the threads is, as a matter of course, a very important property of silk, the manner of working it not only depending on it, but also the durability of the products manufactured from it.

Thus far no artificial silk possessing more than one-half the tenacity of genuine silk has been produced. The com-

pilation given below shows the tenacity of different varieties of silk :

Genuine silk	100
Chardonnet silk	44
Vivier silk	29
Pauly silk	45 to 50
Lehner silk	68

Dr. Hassack has made numerous investigations as regards the moisture and hygroscopicity of artificial silks, as well as the products themselves in general, and from his voluminous work on this subject, the most important data are here given.

The results of the determination of moisture calculated to 100 grammes (3.52 ozs.) dry substance, were as follows :

	Content of moisture in per cent.
Indian raw silk	8.71
Près de Vaux silk	11.11
Fismes silk	10.92
Walston silk	11.32
Lehner silk from Glattbrugg	11.45
Dr. Pauly's cellulose-silk	9.20
Gelatine silk	13.98

The hygroscopicity of the silks was determined by allowing the dried and weighed samples to remain for 24 hours in air completely saturated with steam, when they were again weighed. The absorption of water in per cent. was as follows :

Italian raw silk	20.11
Près de Vaux silk	27.46
Fismes silk	27.12
Walston silk	28.94
Lehner silk from Glattbrugg	26.45
Cellulose silk	23.08
Gelatine silk	45.56

The specific gravity of artificial silks approaches quite closely that of genuine silk, gelatine silk almost correspond-

ing with it, while that of the other is 10 to 11 per cent. greater.

ELASTICITY AND TENACITY OF ARTIFICIAL SILK.

These investigations, of great importance for the utilization of artificial textile fibres, were made by Dr. Hassack in the following manner:

Pieces of thread of genuine silk and of the silk to be tested were placed in the tearing apparatus in such a way, that a free thread 3.93 inches long was lying between the two binding screws, and the length of the thread just placed in the apparatus without being stretched was accurately measured. The tension was then increased till the thread broke, and the length of the piece of thread at the moment of breaking was again measured, the figures showing the load at the moment of breaking, as indicated by the instrument, being at the same time noted. After every test one of the pieces of thread was placed under the microscope, and the number of fibres composing it were counted, so as to be able to determine the separate factors for a single spinning fibre.

To avoid errors every determination was five or six times repeated, and the arithmetical mean of the results taken. The claim of being correct may therefore be made for the figures given below. The results were for:

Genuine silk (Piemont-Organtin)	21.6 per cent.
Chardonnet silk from Près de Vaux	8.0 "
Collodion silk from Fismes	11.6 "
Collodion silk from Walston	7.9 "
Lehner silk	7.5 "
Pauly's cellulose silk	12.5 "
Gelatine silk	3.8 "

The mean results obtained by the breaking tests are given in the table below. In order to be able to compare them with those obtained with genuine silk, the figures referring to the latter have been added. The silk tested

was of medium tenacity and the titer 22 to 24 den.* In the last column of the table the relative tearing resistance of the samples examined, is calculated to the unit titer of 100 den.

Variety.	Titer in den.	Relative breaking resistance.	Calculated to titer of 100 den.	Expressed in per cent. Genuine silk = 100.
		g.	g.	per cent.
Genuine silk . . .	22 to 24	57.5	250	100
Chardonnet silk .	about 80	74.2	92	37
Fismes silk . . .	about 100	71.7	72	28
Walston silk . . .	about 120	151.4	125	50
Lehner silk . . .	110 to 135	171.8	141	56
Cellulose silk . .	about 120	197.6	163	66
Gelatine silk . . .	about 100	63.0	63	25

BEHAVIOR OF ARTIFICIAL SILK IN A CHEMICAL RESPECT.

Chemically artificial silks differ very essentially from the genuine product, but with the sole exception of threads prepared from gelatine, they quite agree one with the other as regards their behavior towards chemical reagents. The examination of artificial silk in a chemical respect is generally made with the assistance of the microscope, it being possible with this instrument immediately to distinguish artificial silk alongside of genuine silk or another fibre in a tissue.

The principal difference, as regards their chemical behavior, between the different kinds of artificial silk known at present, depends on the mode of their preparation, and

*1 den. (1 denier) = 0.10 g. per 1000 m. length of thread.

the difference between silk consisting of pure cellulose—Pauly's silk and viscose silk—and that made from nitro-cellulose has above all to be determined.

When a sample of the threads under the microscope is touched with solution of diphenylamine in concentrated sulphuric acid, threads prepared from nitro-cellulose are immediately colored intensely blue, because none of these silks are ever entirely denitrated. This reaction is so distinct as to be plainly perceptible even with artificial silk which has been dyed. Artificial silk of pure cellulose is entirely indifferent towards this reagent.

When artificial silk, swelled up by having lain in water, is moistened under the microscope with absolute alcohol or concentrated glycerin, it rapidly regains its original volume in consequence of the absorption of water from it.

Swelled-up threads of artificial silk, especially such as have, in addition, been boiled in water, can be readily mashed with the object-glass and broken, this being especially the case with gelatine silk.

Artificial silk when touched with concentrated sulphuric acid is dissolved, solution taking place quite rapidly with nitro-cellulose silk, while threads of pure cellulose first swell up very much, then constantly become thinner, and finally disappear entirely. In the commencement of the action of the sulphuric acid, cellulose silk exhibits plainly perceptible longitudinal streaks. Gelatine threads at first shrink up very much by the action of sulphuric acid, then swell up, though not to a great extent, and dissolve only when strongly heated with the sulphuric acid. By concentrated hydrochloric acid, fibrils are gradually detached from nitro-cellulose silk ; the threads when boiled with it show longitudinal and cross rents, and can be broken into small sharp-cornered pieces when pressed with the object-glass. Gelatine silk is rapidly attacked by hydrochloric acid and in a short time dissolved by it. By acetic acid, cellulose silk, as well as collodion silk, is swelled up, while gelatine silk is completely dissolved by it.

All kinds of artificial silk are in a short time dissolved at the ordinary temperature by half-saturated chromic acid solution, the fluid acquiring a brown color. Genuine silk, to be sure, is also dissolved by this reagent, but considerably more time is required than for artificial silk. Vegetable fibres not being attacked by chromic acid, it can in this manner be at once determined whether only the woof of a piece of tissue of silk-like appearance consists of artificial silk (or genuine silk), and the warp of threads of vegetable origin.

Concentrated soda or potash lye causes cellulose silk, as well as collodion silk, to swell up very much without solution being effected even after continued boiling. The fluid, however, is colored yellow. Genuine silk, when treated with a concentrated alkaline solution, dissolves at the boiling point, the solution, however, remaining colorless. Gelatine silk shrinks up very much, and then passes very rapidly into solution.

Genuine silk, collodion silk and cellulose silk, when treated with cuprammonium solution, swell up very much in the fluid, and then pass gradually into solution. With threads consisting of nitro-cellulose, the small bubbles almost always occurring in artificial silk are plainly visible. Cellulose silk swells up very slowly, and the longitudinal and cross streaks are more distinctly recognized than is the case in water; finally, complete solution takes place. Gelatine silk is not dissolved by cuprammonium, but is colored pale violet.

Cellulose and nitro-cellulose silks may also be plainly distinguished from genuine silk by treating the threads with alkaline cupric oxide (glycerin) solution. Genuine silk is immediately dissolved when heated together with this fluid to 176° F. Genuine Tussah silk requires somewhat longer for solution—about one minute—gelatine silk acting in the same manner. Nitro-cellulose silk and pure cellulose silk are entirely indifferent towards this reagent.

Solution of iodine in potassium iodide solution colors all varieties of artificial silk intensely red to brown, the coloration, however, disappearing by subsequent treatment with water, though nitro-cellulose silk exhibits thereby a transient blue-gray color. With the use of iodine solution and dilute sulphuric acid, genuine silk is colored yellow by the fluid; nitro-cellulose silk acquires a deep blue color shading into violet, while cellulose is colored pure blue. Gelatine silk is colored yellow-brown to red-brown.

Iodine zinc chloride solution colors genuine silk yellow, and collodion silk blue-violet, while cellulose silk only acquires a gray-blue to gray-violet color. Gelatine silk is colored yellow like genuine silk, but falls immediately to pieces, while the structure of genuine silk remains intact.

Cellulose silk burns in somewhat the same manner as pure cotton, and leaves scarcely any residue, while collodion silk leaves behind a small quantity of pure white or gray ash. Gelatine silk when burning gives off vapors of the same disagreeable odor as those evolved by burning glue.

XII.

CELLULOID.

This peculiar substance was first prepared, in 1869, by Hyatt, of Newark, New Jersey, and the original process used by him is said to be at present employed—though probably with many modifications—in many factories.

Celluloid is distinguished by various properties which render it available for many industrial purposes, and there is scarcely another substance so well adapted for the imitation of various bodies; such as tortoise shell, ivory, coral, etc. These imitations can be made in such perfection that, judging solely by their appearance, they frequently cannot be distinguished from the genuine bodies. In addition to these applications, which relate more or less to the production of fancy articles, celluloid has found its way into several industries. It forms at present a very important material in the manufacture of sets of artificial teeth, and it is also frequently made use of for the production of clichés.

Although the physical properties of celluloid are accurately known, its chemical nature is thus far not understood, it being uncertain whether it is a chemical combination at all, or only a mixture of certain bodies possessing the peculiar physical properties on which depends its great applicability. Hence, from the present state of our knowledge, celluloid has to be considered an intimate mixture of the substances used in its preparation. However, it may here be remarked that the nitro-cellulose contained in celluloid, strange to say, loses entirely its explosive power, and is simply inflammable.

Celluloid consists essentially of an intimate mixture of

soluble nitro-cellulose (collodion gun-cotton) with camphor. As the mixture permanently retains the penetrating odor of camphor, the use of the product for various purposes is made impossible, and it has been sought to replace the camphor by substances entirely odorless or of a less intense odor. This object has been partially attained, and celluloid masses entirely free from odor are at present prepared.

Several methods for the preparation of celluloid are known, and they may be designated as dry and wet processes. According to the dry process which was used by Hyatt, the substances constituting the mass are simply combined by mechanical means—kneading, rolling and pressing. In the wet process, fluids capable of dissolving collodion-cotton as well as camphor are used. When the solutions have been prepared, the solvent is allowed to evaporate, whereby the celluloid remains behind, and is then further worked by mechanical means.

As regards the value of the separate methods, it may be said, that they all yield a product of equal quality and it is only a question of which is the cheapest. The purely mechanical process has the undisputable drawback of a number of quite complicated machines being required, and working the masses takes considerable time and power.

The process, in which the substances to be combined are used in the form of solutions, requires but a small expenditure of power; however, a very large portion of the solvent is unavoidably lost by evaporation.

With the use of suitable auxiliary contrivances, the loss of solvent by evaporation may be considerably reduced by condensing the greater portion of the vapors to fluid, as will be explained below, and for this reason the wet process would appear to deserve the preference.

Although various methods for the preparation of celluloid have, in the course of time, become known, most of them have proved to be only immaterial modifications of the main process. The manufacturers very likely introduced these

modifications simply for the purpose of not coming in conflict with the owners of the patents for the fabrication of celluloid according to one of the chief processes.

With regard to the methods used for the manufacture of celluloid, we may distinguish:

1. *The dry method* or *Hyatt's process.* In this method the wet soluble nitro-cellulose is by rolling combined with camphor to a homogeneous mass.

2. *The wet methods.* According to the solvent employed, several methods may be distinguished, namely:

a. Magnus's process. This is based upon dissolving collodion-cotton and camphor in ether, and evaporating the ether by heating the solution.

b. Process employed by the factory at Stains, near Paris. This is based upon the fact that collodion-cotton and camphor are also soluble in methyl alcohol, and that the latter may therefore be used to effect solution. By both of these wet processes, celluloid is obtained which in itself is very homogeneous and requires mechanical manipulation only for a short time to render it fit for further working.

PREPARATION OF THE COLLODION-COTTON.

The principal requisite for the manufacture of celluloid is the use of a nitro-cellulose completely soluble in the known solvent. As regards the preparation of such a product, the reader is referred to what has been said in this respect in describing the manufacture of artificial silk according to Chardonnet's method. It may be repeated that in working according to one of the wet processes, the use of a perfectly soluble product is of the utmost importance.

When working with freshly prepared collodion cotton, its complete solubility has to be ascertained by treating a small sample with the solvent. If the test shows the collodion cotton not to be completely soluble, it may nevertheless be used for the manufacture of celluloid, but the solution must by all means be filtered, though filtration need not be so

thorough as when the collodion is to be used for the manufacture of threads. For the purpose of filtration it suffices to force the solution under slight pressure through a layer of cellulose, 0.59 to 0.78 inch thick, in order to obtain a fluid in which the camphor may be dissolved.

According to the original statements by Hyatt, collodion-cotton suitable for the purpose of preparing celluloid can only be obtained by using for nitration an extraordinarily fine quality of paper consisting of pure cellulose. Hyatt is said to have employed for this purpose the finest quality of tissue-paper torn into small pieces by a special machine. These pieces were then treated with nitrating fluid.

It will be readily understood that with the use of such an expensive raw material as a fine quality of tissue-paper, the cost of producing collodion-cotton would be very much increased, and it would be impossible to furnish celluloid articles at the low price at which they are at present brought into commerce. It has, however, been shown that for the manufacture of celluloid, collodion-cotton prepared from any kind of cellulose may be used, provided the latter has been subjected to sufficient purification.

PREPARATION OF CELLULOID ACCORDING TO HYATT.

The collodion-cotton, carefully freed from acid, is as far as possible dehydrated by the use of a powerful press, then reduced, and completely dried. It is not stated how drying is to be effected, but the process described for the preparation of nitro-cellulose may be employed. The dry collodion-cotton is carefully triturated, mixed with camphor and subjected to further treatment by mechanical means. This account, as will be seen, gives a very meagre description of the manufacture of celluloid, no data regarding the manner of mixing the collodion-cotton with the camphor being furnished, nor is any reference made as to the proportions in which the materials are to be mixed. A somewhat better insight into Hyatt's process is afforded by the following description :

The collodion-cotton previously carefully washed is ground fine in a hollander, and converted into quite a solid cake by removing the water by pressure. This cake is again reduced and mixed, under water, with camphor. Mixture being complete, the mass is kneaded and rolled by mechanical means. The object of this manipulation is probably to bring the particles of collodion-cotton and camphor into still more intimate contact, and, in addition, to cause evaporation of a large portion of the water contained in the mass. The latter having now become quite solid, is subjected to a very high pressure whereby more water is removed, and the combination of the nitro-cellulose with the camphor completed.

The mass is contained in a jacketed cylinder, the bottom of which is formed by the piston of a hydraulic press. While the latter is at work, steam is introduced into the space between the jacket and the cylinder, and the temperature is gradually raised till the contents of the cylinder are heated to 266° F. Although at this temperature camphor has already great tendency towards vaporization, by reason of the state of fine division in which it is, in consequence of the previous operation, the vapors evolved can only spread to the particles of collodion-cotton lying next to them. Hence, this treatment at a higher temperature and at a high pressure can probably be only viewed in the light of making the mass finally and completely homogeneous.

With the use of a mixture consisting only of collodion-cotton and camphor, the cylinder, when the above-mentioned temperature has been reached, contains a colorless mass. In the hot state, this mass possesses a very high degree of plasticity, but on cooling to the ordinary temperature, becomes firm and quite hard. In the state in which it comes from the hydraulic press it can be rolled out to plates of any thickness, or pressed in moulds, being left in the latter till cooled to the ordinary temperature.

Celluloid being a substance which can be dyed any desired color, as well as mixed with pulverulent materials, articles differing very much in appearance may be made from it. The admixture of the foreign bodies may be effected previous to bringing the mass into the hot press, or when it is taken from the latter. In the latter case, the celluloid is rolled out into thin plates upon which the pulverulent substances are scattered, and rolling is repeated until a perfectly homogeneous mass is obtained.

Regarding the quantities of the two fundamental constituents of celluloid, it may be stated that for every two parts of collodion-cotton one part of camphor is said to be used.

PREPARATION OF CELLULOID ACCORDING TO TRIBOUILLET AND BESANCÈLE.

According to this method, which, in a certain sense, appears to be an improvement on Hyatt's process, 100 parts of collodion-cotton are very intimately mixed with 42 to 50 parts of camphor.* The mass is then wrapped in very strong press-cloths, and brought into a hot-press, very similar in construction to that used in candle factories for pressing oleic acid from crude acid cakes. The masses to be pressed lie between hollow iron prisms heated by steam, and by means of a hydraulic press the whole is pressed together to the same extent as the press-cakes become thinner. The press is enclosed in a box, and the latter is connected by means of a pipe with a cooled space in which the vapors escaping from the hot pressed mass are condensed. In pressing the mixture of collodion-cotton and camphor, the escaping vapors can only consist of water and camphor, and the object of this arrangement seems to be to recover the camphor present in excess.

* Although it is not thus stated, mixture is probably effected in a wet state in a hollander.

After remaining for several hours in the press, the cakes are brought into a box upon the bottom of which stands a vessel containing a substance having great affinity for water—calcium chloride or sulphuric acid—and the air in the vessel is then exhausted. The mass is thus completely dried, and the preparation of the celluloid finished. According to the present state of the industry, all the processes for the production of celluloid by purely mechanical means may be designated as obsolete, and, in all probability, they have generally been abandoned. Although it is a fact that by the presence of the camphor the nitro-cellulose is deprived of its explosive power, it cannot be denied that such is the case only when the mixture is sufficiently intimate. However, such an intimate mixture is only effected towards the final stages of the manufacturing process, and up to that period the operation is by no means free from danger, if care is not taken that the mass up to the time of hot-pressing contains enough water to render explosion impossible.

PREPARATION OF CELLULOID WITH ALCOHOLIC CAMPHOR SOLUTION.

This process yields good results, and is said to possess the great advantage of all danger of explosion being excluded —which, however, may be doubted. The collodion-cotton is prepared by grinding, and is then freed as far as possible from water, when solution of camphor in strong alcohol is poured over it, the solution being brought in contact with all portions of the collodion-cotton by vigorous manipulation of the mass.

The mass is then heated in a closed vessel under pressure. Alcohol boiling at a temperature far below the boiling point of water, it will be impossible to reach in such a vessel a temperature of 266° F., at which the formation of celluloid is said to take place. Heating should probably not be carried beyond a point at which complete solution of the collodion-cotton in the alcoholic camphor solution is

effected. While collodion-cotton does not dissolve in alcohol at the ordinary pressure, solution is effected by heating it together with alcohol under a certain pressure.

When solution is complete, the mass is allowed to remain in the closed vessel until cooled to the ordinary temperature. It forms a gelatinous substance consisting of celluloid saturated with alcohol and water. For the removal of the latter, heat cannot be applied as otherwise the surface which solidifies first would be full of bubbles caused by the vapors being unable to escape through the viscous mass. Hence, in order to obtain a uniform product free from bubbles, the soft celluloid mass will have to be cut up into thin slices, and the latter dried in a warm room. Drying requires quite a long time, and all the alcohol used is lost. When a piece not thoroughly dry is tested with a knife, the outside will be found quite solid while inside it is of a lardaceous nature. By immersing the dry pieces in hot water, they can be made soft and plastic, and by rolling readily combined to a homogeneous mass.

PREPARATION OF CELLULOID ACCORDING TO MAGNUS.

The process introduced by Magnus, of Berlin, for the preparation of celluloid is perhaps the most rational one of all the wet methods, because with the exercise of sufficient care all danger of explosion or fire is excluded.

The description of Magnus's process, which has become public, is also very meagre, and it may be seen at the first glance that it contains only the principle of the entire process, but that its technical execution will probably have to be effected in a less simple manner.

According to law, collodion-cotton as brought into commerce must contain at least 25 per cent. of water, the possibility of explosion being only excluded under these conditions. Now, it has been stated, that in the Magnus factory, the wet, compressed collodion-cotton is separated and dried upon hot iron plates(!). An explosion of collodion-cotton thus treated could in all probability scarcely be avoided.

The mode of preparing the solution of dry collodion-cotton is as follows: Over 50 parts by weight of collodion-cotton is poured a mixture of 100 parts by weight of ether and 5 parts by volume of alcohol of 0.728 specific gravity, 28 parts by weight of camphor having been previously dissolved in this mixture. Stone-ware pots covered with a loaded rubber plate are used for dissolving purposes. The mass is from time to time stirred till solution is complete and the pots contain a gelatinous mass. It is further stated that this mass becomes plastic after some time by manipulation between rolls, and that plates may be prepared from it which are kept till, by the evaporation of the greater portion of the ether, they have become hard enough to be pressed, the latter operation being effected in hot presses, and the quality of the celluloid is said to be the better, the more sharply the plates are pressed.

According to another process which differs but little from the one described above, in place of ether, methyl alcohol in which the required quantity of camphor has been dissolved is used as a solvent for the collodion-cotton.

PREPARATION OF CELLULOID WITH RECOVERY OF THE SOLVENT.

It must appear strange to any one conversant with chemical principles, how incomplete and, in certain respects, very singular, are the descriptions given above for the preparation of celluloid. It is, therefore, considered advisable to give here a description of a process which can be practically applied, it being without danger and allowing of the recovery of the quite expensive solvents.

With reference to the basis-material of the entire celluloid manufacture, namely, collodion-cotton, it may be said that, while it could probably be obtained from different manufacturers of chemical products, it would be preferable to prepare it in the celluloid plant itself, because by this means

a product would be obtained which, as regards complete solubility, answers all demands. In a larger plant producing annually large quantities of celluloid articles, the preparation of collodion-cotton in the plant itself would also appear advisable from an economical standpoint.

In describing the manufacture of artificial silk according to Chardonnet's method, attention has been drawn to the great care bestowed upon the production of nitro-cellulose which is completely soluble, and collodion-cotton possessing this property being also required for the manufacture of celluloid, the reader is referred to the process used by Chardonnet. When a freshly-prepared quantity of collodion-cotton is to be worked, it is, in all cases, advisable to test a sample of it as to its solubility. For this purpose a small quantity of the collodion-cotton is thoroughly dried. One gramme (15.43 grains) of the dry mass is brought into a large test-tube and 200 cubic centimeters (12.2 cubic inches) of ether are poured over it. Solution is hastened by continued shaking, and the test-tube is then placed perpendicularly in a place protected from shocks.

In the course of 24 hours, the contents of the test-tube should form a clear, transparent fluid, which is a proof of the entire quantity of collodion-cotton having been dissolved in the ether. If an opalescent layer appears on the bottom of the test-tube, it consists of nitro-cellulose swollen up but not dissolved. The quantity of this can be readily determined by quickly filtering the fluid, washing the residue remaining upon the filter with ether, drying and weighing it. By deducting the weight of the filter, the quantity of nitro-cellulose which has remained undissolved is found.

It may here be remarked that perfectly colorless celluloid can under no conditions be produced from incompletely-dissolved collodion-cotton, though the latter may be used for opaque or intensely colored celluloid articles.

Collodion-cotton to be dissolved must be perfectly free

from water. The wet material is separated as far as possible to a flocculent mass resembling wadding and, after spreading it out in thin layers upon metal plates, is dried with the use of the same precautionary measures as described in detail in the manufacture of nitro-cellulose.

The drying plant need not be of large size, and it should be laid down, as a rule, not to dry more collodion-cotton at one time than is to be dissolved the same day. By proceeding in this manner all danger which may also arise from entirely dry collodion-cotton is excluded.

The apparatus in which the solution of the collodion cotton and camphor is effected, as well as the preparation of the fluid celluloid, consists of an iron cylinder which may be constructed of ordinary boiler-plate, but has to be well tinned inside. The head of the cylinder is provided with an aperture, which can be closed air-tight, for the introduction of the solid materials, while on one of the sides the cylinder is furnished with a pipe for the admission of the solvent. Through the centre of the head of the cylinder passes the shaft of a stirrer which carries a spiral of tinned sheet-iron. The bottom of the cylinder is furnished with a discharge pipe for the finished solution, and one side is fitted with a small cock for taking samples of the fluid.

The manner of working with this apparatus is as follows: The quantity of camphor intended for the operation is first introduced, and then the dry collodion-cotton, when the cylinder is closed and the stirrer slowly set in motion, the solvent being at the same time admitted through the side-pipe. The stirrer is uninterruptedly kept in slow motion, the formation of masses which are simply swollen and impede solution being thereby prevented. The stirrer is only stopped when it is shown by samples taken from time to time that solution is complete.

As regards the solvent to be used there is, in our opinion, but one which is actually entirely suitable, namely, pure anhydrous ether. Solution of the collodion-cotton may

possibly be hastened by mixtures of ether and alcohol, it being asserted by some that such is the case, but they exert an injurious influence in working the celluloid masses.

Pure ether boils at 96.8° F.; absolute alcohol at 172.4° F., and the small quantity of water contained in alcohol when not absolute, only at 212° F. When the finished solution is brought in contact with air, the ether of all the fluids present will, of course, evaporate first, so that after a certain time the mass contains almost no ether whatever, but nearly the entire quantity of alcohol, and most certainly all the water. For the evaporation of the alcohol greater heat will have to be used and the alcoholic vapors evolved, and later on the aqueous vapors also, will form in the mass, which has in the meantime become viscous, bubbles which cause the celluloid plates to bulge and can only with difficulty be removed by rolling. Hence to avoid all difficulties in working, dry collodion-cotton and anhydrous ether should only be used.

The recovery of the ether evaporating from the fluid celluloid mass has generally been declared impossible, so that it is simply allowed to escape in the form of vapor into the air. This procedure, however, has many disadvantages, the cost of production being, on the one hand, increased, and on the other, it leads to many inconveniences in the manufacture itself. By being constantly in an atmosphere impregnated with vapors of ether, the health of the workmen is likely to be impaired, and in factories working in this manner, the workrooms should always be kept thoroughly aired. Another drawback is the great danger from fire, as by the mere striking of a match, the mixture of air and ether-vapor might be ignited and cause a fearful explosion.

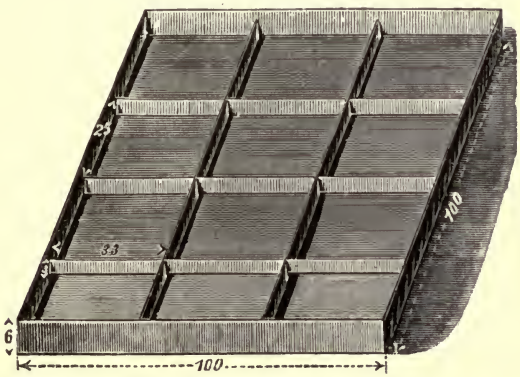
RECOVERY OF THE ETHER.

By working according to the method described below, almost the entire quantity of ether used for the preparation

of the celluloid solution may be recovered, the cost of production thus being considerably reduced. The odor of ether can scarcely be noticed in the factory, and there is no danger from fire, and injury to the health of the workmen is excluded.

An apparatus of the following construction is used: The clear solution of celluloid mass prepared in the manner above described, is brought into a sheet-iron cylinder tinned inside, and provided on the top with a gutter 4 to 6 inches deep, into which fits the rim of the lid. In the latter is fitted a small cock, and above the bottom of the cylinder is

FIG. 36.



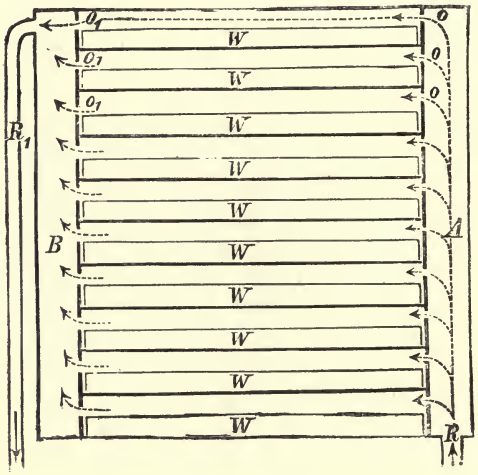
a pipe with a stop-cock, which serves for the discharge of the fluid. The solution to be worked is introduced through a pipe furnished with a stop-cock, which enters the cylinder at a slight distance below the gutter. The latter is kept filled with water, the hydraulic joint thus formed preventing the escape of ether-vapor. By this arrangement the interior of the cylinder is accessible without difficulty. When the cylinder is to be filled with solution, the small cock fitted in the lid is opened to allow the escape of air.

For the purpose of solidifying the solution, a shallow tray of the shape shown in Fig. 36 is used. It is constructed of

tinned sheet-iron and measures 39.37 inches in length and width, and 2.36 inches in depth. It is divided into 12 or 15 compartments by partitions 1.18 inches high, so that each compartment is 12.99 inches long, 7.87 (or 9.84) inches wide, and 2.36 inches deep.

Ten such trays *W*, may be placed one above the other, in the ten compartments of a wooden box shown in section in Fig. 37. On the right of this box is a small box *A*, com-

Fig. 37.



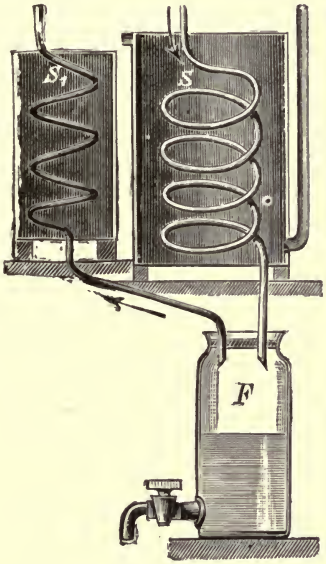
municating below with the pipe *R*, and connected by means of the narrow longitudinal slits *o*, with the separate compartments in which the trays stand. On the left of the box is another small box *B*, of the same construction as *A*, and connected with the pipe *R*.

The pipe R_1 communicates with the apparatus for condensing the ether-vapors, its arrangement being shown in Fig. 38. The pipe R_1 terminates in a long, wide tin coil *S*, lying in a vat kept constantly full of cold water. The lower end of the coil passes into the neck of a large flask *F*, fitted near the bottom with a cock through which the condensed ether is drawn off. A narrower pipe S_1 made

into a coil in a vessel filled with ice and passing out free, branches off from the neck of the flask *F*.

The operation of preparing solid celluloid with this apparatus is as follows: One of the trays *W*, is filled up to a mark 1.97 inches above its bottom with solution from the cylinder, and placed in the uppermost compartment of the box. The other trays having in the same manner been filled with solution are then successively placed in the com-

Fig. 38.



partments of the box, and the door of the latter is closed air-tight.

By means of a small ventilator, a constant current of warm air is slowly conducted through the pipe *R*, into the box. This current of air is produced as follows: In a room underneath the workroom, and entirely isolated from it, a boiler is bricked in an ordinary fire-place. In this boiler, which is filled with water, lies a tin coil open on one end and connected on the other, with the ventilator which com-

municates with the pipe *R*, extending through the floor of the workroom. When the water in the boiler has been brought to the boiling-point, the air in the coil becomes heated, is sucked off by the ventilator, and replaced by fresh air flowing in, so that there is constantly a current of warm air in the pipe *R*. The course of the operation is so regulated that the current of air moves slowly, and that its temperature never exceeds 86° to 89.6° F. Ether boils at 96.8° F., and should the temperature of the air become that high, the mass in the trays might be brought to the boiling point and in solidifying be interspersed with bubbles. The current of warm air enters through the narrow slits *o*, by means of which the box *A* is connected with the compartments in which the trays stand, and in passing to and fro over the surface of the fluid, becomes impregnated with the vapors of the ether. It then enters the box *B*, and passes through the pipe R_1 into the coil S_1 which is surrounded by cold water. The greater portion of the ether contained in the air condenses to fluid and collects in the flask *F*, from which it is from time to time drawn off. The air escaping from *F*, can only pass out through the coil S_1 which terminates outside the workroom. The coil S_1 lying in the vessel filled with ice, the last traces of ether are condensed and run back into the flask *F*.

With the use of these contrivances, the evaporation of the ether in the celluloid solution is very rapidly effected, and the contents of the trays are gradually converted into a mass somewhat resembling congealing glue. The depth of the layer of fluid in the tray, which was originally 1.97 inches, having been constantly reduced by the evaporation of ether, and the height of the partitions being but 1.18 inches, each compartment, when evaporation has progressed to a certain degree, will contain a body representing, when the mass has become perfectly dry, a prism 12.99 inches long, 7.87 inches wide, and about 0.98 inch thick. When drying is finished, each of these prisms may be obtained by

itself by turning the tray upside down, and the dimensions of these prisms are just right to allow of their being conveniently worked with suitable rolls. Drying of the celluloid mass may be considered complete, when a sample prism taken from one of the trays can be cut like quite solid cheese.

THE DRYING CHAMBER.

The prisms taken from the trays are placed in a drying chamber heated by warm air and provided with a pipe terminating either in the open air or in a chimney. The temperature of the chamber may be 104° to 113° F., the last traces of ether still adhering to the mass being thereby evaporated. The drying chamber is furnished with frames covered with nets of stout twine upon which the prisms are placed so that they rest upon one of their narrow longitudinal sides. They remain in the drying chamber till they form a hard, horn-like mass, and the fracture of a broken piece presents a perfectly uniform appearance, a lardaceous appearance of the fracture being indicative of insufficient drying.

If the crude celluloid is to be rolled, it has to be heated to acquire sufficient plasticity, and the drying chamber may also be used for this purpose. When drying is finished a current of air having a temperature of 140° to 158° F. is conducted into the chamber, this temperature sufficing to give to the celluloid the required softness. One plate after the other may then be taken from the chamber and passed through the rolls.

The preparation of celluloid with the assistance of the contrivances described above, presents many material advantages, it being possible to prepare in a short time in a small room larger quantities of celluloid, and recover almost the entire quantity of ether required for making the solution. The workmen are not exposed to the vapors of ether, and there is no danger from fire during the entire operation.

The plates of crude celluloid obtained by the above-described method are either entirely colorless or of a slightly yellowish color. However, even if they show the latter color, they should be perfectly uniform throughout their entire bulk, dull and cloudy spots imbedded in the transparent mass being indicative of the solution used having contained particles of nitro-cellulose only swollen but not dissolved. As previously mentioned, such defective celluloid may be used for the preparation of masses which are to be colored, or filled. Dull spots may sometimes disappear by long-continued rolling.

The dried material does not yet possess the great hardness and elasticity characteristic of celluloid, it acquiring these properties only by mechanical manipulation, the first step being rolling, and the more frequently this operation is repeated and the greater the pressure applied, the better the quality of the product will be. It would therefore seem that by this purely mechanical process, a change in the position of the finest particles of the celluloid is effected.

PROPERTIES OF CELLULOID.

Celluloid prepared in a proper manner forms, as previously mentioned, a colorless or very slightly yellow mass closely resembling horn, or still more so, tortoise shell. It represents a mass with a slight odor of camphor, becoming, however, in the course of time entirely odorless by reason of the evaporation of the particles of camphor lying near its surface. By vigorously rubbing or heating an article of celluloid, the odor of camphor becomes more pronounced.

At the ordinary temperature, rolled celluloid is very hard and extraordinarily elastic, and thicker pieces of it can scarcely be broken. It may be sawed, planed and turned in the lathe like fine-grained wood. A thin plate of it may be cut with the scissors, it behaving in this respect, somewhat like very solid cardboard.

Celluloid, firm and brittle as it is at the ordinary tem-

perature, may by suitable heating be changed into a very plastic mass which can be moulded into any desired shape.

Celluloid being a bad conductor of heat, larger pieces of it to be rendered plastic have to be for a longer time exposed to an adequate heat, otherwise they would offer too much resistance in rolling or pressing. Celluloid becoming quite plastic at a temperature of 158° F., pieces of it are most conveniently worked by throwing them in a vessel full of boiling water, covering the vessel, and allowing the whole to stand quietly for some time, when by samples taken from the vessel it is ascertained whether the pieces are sufficiently plastic.

The plasticity of celluloid increases considerably at a higher temperature. When heated to between 248° and 302° F., it is as plastic as wax, and like it, can be given any shape desired by pressing it in a mould, or two pieces of the hot mass may be made into one by pressure.

If heating the cellulose be effected so that the rise in the temperature can be accurately determined, it will be noticed that up to nearly 284° F. no other change takes place besides greater softness and plasticity. If, however, the temperature be increased to 284° F., a molecular change takes place; the mass suddenly becomes opaque, and by slightly raising the temperature, at the utmost to 293° F., spontaneous decomposition sets in. The mass puffs up very much and decomposes, a heavy smoke being evolved. However, there is no explosion, this being a proof that the celluloid no longer contains nitro-cellulose.

On coming in contact with a burning body, celluloid ignites very readily, and burns with a yellow, luminous, sooty flame, the odor of camphor, caused by the evaporation of this substance being very pronounced. When the flame of the burning celluloid is blown out, combustion continues very rapidly without flame, vapors of camphor ascending constantly from the glowing mass. The process which thereby takes place consists in that the nitro-cellulose, by

reason of its high content of oxygen, continues to burn, and the camphor evaporates in consequence of the heat developed, the temperature being, however, not sufficiently high for the ignition of the camphor vapors.

Towards solvents, celluloid behaves quite indifferently. In water it remains entirely unchanged and, by reason of this property, it is used for making syringes, basins, etc., for surgical purposes. When placed for some time in strong alcohol, it swells up very much, but does not dissolve, solution being gradually effected only by the addition of ether. By being allowed to stand in the air, the solution yields celluloid with its original properties. When left for a longer time in contact with sulphuric acid, it is completely dissolved, and concentrated nitric acid dissolves it without residue. By concentrated soda lye it is only dissolved when remaining for a longer time in contact with it.

The physical properties of celluloid are the same as those of horn, wood and wax. In mechanical manipulations such as cutting, sawing, planing, turning, it can be treated just like horn or wood, and in fact behaves to better advantage for the operator as, being a structureless substance, it can in the same manner be worked in every direction. Like wax, it possesses the property of being by heat converted into a very plastic substance which can readily be brought into any desired form. It commences to become plastic at about 122° F., and plates of it heated to this temperature may be rolled under strong pressure. At a higher temperature its plasticity increases considerably and, as a rule, one of 212° F. suffices for all kinds of operations by rolling or pressing. At 248° F. it becomes soft enough to allow of two pieces being made into one by kneading.

One of the most prominent properties of celluloid is its great tenacity combined with uncommonly great elasticity. A stick of it as thick as a finger can at the ordinary temperature be bent to and fro, regaining its original form when the tension ceases; no flaws or cracks are formed

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even by frequently repeated bending, and such a stick can scarcely be broken. However, when exposed to a very low temperature celluloid has a tendency to become brittle.

WORKING CELLULOID.

The masses obtained by completely drying the pieces and by evaporating celluloid solutions, do not show the great hardness, elasticity and high lustre possessed by articles prepared from them, but are of a more or less soft nature, having in this respect a certain resemblance to not entirely dried gelatine. These properties appear only by vigorous mechanical manipulation, a change in the position of the smallest particles of the mass being probably effected, or they are more closely drawn together than is the case in the mass when simply dried.

The mechanical manipulation of celluloid should always commence with rolling the plates. For this purpose, the sufficiently dried plates are heated in the drying chamber to between 140° and 158° F., and thrown into hot water where they are allowed to remain till heated throughout. It is of great importance that the plates should be heated throughout their entire thickness, as otherwise they would tear laterally under the rolls.

For the purpose of rolling, smooth steel rolls, so arranged that the distance between them can be regulated at will, are used. In order to be able to carry on the work rapidly, it is advisable to place several such pairs of rolls one behind the other, the rolls of each succeeding pair being more closely set than those of the preceding one, so that the plate which has been drawn out in the first pair of rolls is rapidly converted into a very thin plate. By working in this manner, the plate need only to be heated once, enough heat to keep it sufficiently soft being developed by the pressure.

The thin plates thus obtained are placed together and are sufficiently heated to allow of their being welded together when rolling is repeated. The more frequently roll-

ing is repeated and the greater the pressure, the more tenacious, elastic and lustrous the celluloid will be. According to the purpose to which the celluloid is to be applied, thinner or thicker plates of it are prepared by rolling. For further working these plates are sufficiently heated, and articles prepared from them, as a rule, by stamping or pressing in warmed hollow moulds.

COLORING CELLULOID.

Like artificial silk, celluloid possesses the property of being readily colored, it taking up with special facility the soluble tar colors. If an article of colorless celluloid be only for a short time placed in the solution of a dye-stuff, the surface only will be colored, the interior remaining colorless, but if left in it for a sufficiently long time, it will be colored throughout its entire mass. Even comparatively thick articles appear uniformly colored upon their cross sections if left long enough in the solution. It may, therefore, be supposed that solutions of dye-stuff penetrate the celluloid mass like a sponge, and that the separate particles of the coloring matter are held by the smallest particles of the celluloid mass.

As there are soluble tar-colors of all shades, any desired color may be given to celluloid, and the resulting product is distinguished by being perfectly transparent, very lustrous and smooth, surpassing in this respect the finest quality of colored gelatine.

Transparent celluloid articles are, as a rule, colored a beautiful golden yellow, which is readily produced by placing them in picric acid solution.

Celluloid of any desired color may be readily obtained, and there are several ways of producing articles from the colored material. The most simple way is to color the celluloid while it is being prepared. This is effected by mixing with the celluloid solution when finished, coloring matter soluble in alcohol, the solution being by vigorous

stirring distributed throughout the fluid in order to obtain a uniformly colored product. A certain quantity of celluloid of the same uniform color is thus obtained. However, as celluloid of different colors has to be used for various purposes, this method of direct coloring while preparing the mass, notwithstanding its convenience, is only employed in exceptional cases, it being preferred to color the finished articles.

The simplest plan, as previously mentioned, is to use tar-colors soluble in alcohol, they being readily taken up by the celluloid, and it is only necessary to allow the articles to remain in the solution till they are sufficiently colored. They are then taken out, rinsed in water, and made lustrous by vigorous rubbing with a soft cloth.

However, there is a way of producing certain color effects more beautiful than can be done with tar colors, and below a few hints regarding this manner of coloring are given. In this operation it has to be borne in mind that the coloration depends on the concentration of the solutions used; the more saturated they are, the deeper the coloration will be. It is advisable to learn by a few small experiments the required concentration of the solutions to be used. A *beautiful yellow* may be produced by placing the article first in solution of acetate of lead in water, then slightly rinsing it in clean water, and finally bringing it into a solution of potassium dichromate to which sufficient soda has been added to color it yellow. By this means the beautiful yellow combination known as chrome yellow is formed in the pores of the celluloid.

Red may be produced in various ways. A very beautiful *scarlet* is obtained by placing the articles for a short time in water which has been compounded with a small quantity of nitric acid, and then bringing them into a fluid obtained by treating finely-powdered cochineal with ammonia. When the desired shade of color has been attained, the articles are taken from the solution, and thoroughly rinsed

in water. A *dark, peculiar red* is obtained by treating the articles first with a solution of potassium chromate, and then with a solution of nitrate of silver, the beautiful red silver chromate being thereby formed. A magnificent *purple-red* is obtained by placing the articles in a highly dilute solution of trichloride of gold, and then exposing them to the direct sun light. By the action of the latter the chloride of gold is decomposed and the celluloid colored.

Blue may also be obtained by various means. *Indigo-blue* is produced by simply placing the celluloid in dilute solution of indigo-carmine in water. Another very beautiful blue, the so-called *Berlin-blue*, is obtained by placing the articles in a solution of ferric chloride in water, rinsing, and bringing them into a solution of yellow prussiate of potash.

Green is obtained by placing the celluloid in a solution prepared from 2 parts of verdigris and 1 part of ammonium chloride.

Violet may be produced by first dyeing the articles slightly blue with indigo, and then treating them with cochineal solution till the desired shade of violet appears.

Brown. Prepare a solution of permanganate of potash in water, add to it soda solution so that no precipitate is formed, and place the articles in the fluid.

Gray. Silver-gray is obtained by placing the articles in a very dilute solution of acetate of lead, and then bringing them into an atmosphere of sulphuretted hydrogen. The lead sulphide formed shows a peculiar, metallic, lustrous, gray color. It is, however, absolutely necessary to use, as above mentioned, a very dilute solution of acetate of lead, otherwise the color will be black instead of gray.

Black. Mix solution of logwood extract with solution of tannin in water and allow the articles to remain in the mixture for a few hours. They are then rinsed in water and placed in ferrous sulphate (green vitriol) solution whereby they acquire a deep black color. Another metallic, lustrous black is obtained by placing the articles in nitrate of silver

solution; according to the concentration of the solution the color will be gray to deep black.

PRINTING ON CELLULOID.

By reason of its smooth surface, ordinary printing inks do not adhere well to celluloid and, without special treatment, it would be impossible to print on it in colors.

To make a celluloid plate suitable for being printed on, its surface has to be provided with a fine graining in a manner similar to that in which a lithographic stone is prepared. Celluloid possessing, however, a comparatively slight degree of hardness, graining is effected by means of a small sand blast, the originally lustrous plate becoming thereby matt. The plate is then well washed with water to remove all the celluloid dust, and is then thoroughly dried. It is next coated with a varnish consisting of equal parts of a fine quality of pale linseed-oil varnish and colorless copal varnish diluted with enough oil of turpentine so that the varnish can spread, like collodion, over the plate. The plate is coated with this varnish in exactly the same manner as a glass plate with collodion for photographic purposes. The excess of varnish is allowed to run back into the flask, and the plate is set on edge to dry.

A plate thus prepared can be printed on in the press in various colors, the latter adhering as well as on paper. If, after the colors are dry, the plate is coated with a thick celluloid solution and the latter, when congealed, is polished with a soft, woolen stuff, the printing ink lies under a layer of celluloid, and the plate may be cleansed without fear of effacing the printing.

Celluloid articles may also be provided with pictures of various colors by means of a process closely resembling that employed for the production of the so-called transfer pictures or metachromatypes. According to this process the pictures are in inverted succession printed in colors on thin paper, and the finished impression is finally coated with a mass

which by moistening becomes very sticky. In transferring the pictures to glass, wood, porcelain, etc., this coating is moistened, and the paper, coated side down, is laid upon the article to which it is to be transferred, and firmly pressed against it. After a short time the paper is softened by moistening the back, and is then carefully drawn off, starting from one point. The paper peels off smoothly from the picture, the latter remaining attached to the basis.

If this process is to be applied to the ornamentation of celluloid articles, the colors used for the production of the picture have to be mixed with a body readily soluble in strong alcohol, soft copal finely pulverized being a suitable material for this purpose. When all the colors have been printed, the printed portions of the paper receive an additional impression made with spirit copal varnish, the rest of the paper remaining free.

For the purpose of transferring such a transfer picture to celluloid, the surface of the latter is moistened with strong alcohol, which causes the uppermost layers of the celluloid to swell up, and the paper, picture side down, is laid upon the plate thus prepared. The latter is then covered with a glass plate and the whole placed in a press where it remains for a few hours under slight pressure. When there can be no doubt of the transferred picture adhering firmly and having become dry by the evaporation of the alcohol, the plate may be laid in water, and the paper, when sufficiently softened, carefully drawn off from the picture.

For the protection of the picture and to make it at the same time durable, it may be coated with a layer of celluloid by pouring celluloid solution over it. If imitation gold or silver has been used in printing the pictures, this coating with celluloid is of special importance, because these materials, when exposed to the air soon loose their metallic lustre, and the pictures become unsightly. If, however, the pictures when just finished are provided with a layer of celluloid, no matter how thin, the colors are en-

tirely excluded from the action of the air and retain their metallic lustre.

Printing on celluloid in the same manner as pictures in many colors are produced on paper, has also been recently successfully accomplished by the use of tar colors soluble in concentrated acetic acid, the colors adhering firmly and retaining their sharp outlines without running into each other. These colors, as shown by microscopical examination, strongly attack the celluloid, penetrating to a great depth, in consequence of which they adhere firmly. However, as metals are also attacked with great energy by acetic acid, metallic printing blocks cannot be used in this case, and blocks of a material entirely indifferent towards acetic acid have to be substituted for them, gutta-percha being especially suitable for this purpose. Such printing blocks can be readily made by taking a plaster of Paris cast from the original—an engraved metal plate, or a wood-cut—laying upon it, a gutta-percha plate previously softened in hot water, and subjecting the mould together with the gutta-percha plate to pressure in a press till the gutta-percha has again become hard. The plate then shows all the depressions and elevations of the original plate, and may at once be used for printing.

CELLULOID WITH FILLING MATERIALS.

Celluloid can without difficulty be worked with indifferent bodies into uniform masses, the substances thus obtained possessing, in addition to the hardness and elasticity of celluloid, other properties which make them suitable for the preparation of various specialties.

Although all kinds of perfectly dry substances in a pulverulent form may be used as filling material, white pulverulent bodies are, as a rule employed, the resulting masses being of course opaque.

However, since so-called white bodies are colorless and the effect appearing as white to the eye is simply due to the

peculiar reflection of the light, masses presenting a very characteristic appearance may be prepared from these bodies and from celluloid.

By mixing with the colorless celluloid only a small quantity of the powder of a white body, masses are obtained which, though appearing white, are to a certain degree transparent. Milk poor in fat presenting the same appearance. Masses of this kind are called *milk-white*, and articles of a beautiful milk-white color may be made from celluloid. Ivory also appears translucent, but its color is not pure white, it always showing a yellowish tinge. Now, there is no difficulty whatever in mixing a white pulverulent body in suitable quantity with a yellow one, and by combining this mixture with celluloid, masses are obtained which, as regards color, bear a close resemblance to ivory.

If colorless celluloid be mixed with a suitable quantity of a pure white body, masses resembling in appearance polished white marble are obtained. By the addition of powders of a different shade, the color of such masses may be toned down as much as desired.

The following materials may be used: Magnesia, chalk, talcum or starch. For certain masses which are to be very heavy, artificially prepared barium sulphate (permanent white), or zinc white may be employed.

Celluloid masses of light weight being especially desirable for the manufacture of cane heads, etc., a white powder of slight specific gravity is, as a rule, used as filling material, magnesium powder deserving, in this respect, preference above all others.

The filling material may be combined with the celluloid either in the preparation of the latter itself, or by working it into the finished product.

In working according to the first method, the mixture of the viscous celluloid solution with the powder is best effected in a contrivance resembling in its construction a revolving barrel, it consisting of a tinned sheet-iron cylinder revolv-

ing around its axis. The quantity of the solid body to be used having been introduced, the celluloid solution is allowed to run in, and the cylinder closed air-tight. The cylinder should at the utmost be filled three-quarters full. It is then slowly revolved by means of a mechanical contrivance, the operation being continued till the fluid has combined with the powder to a viscous mass of the appearance of cream.

This fluid is discharged into the vessels in which it is to coagulate and the mass, when solidified, is thoroughly dried, the product obtained being white celluloid plates. In cutting such a plate in two, it will frequently be observed that the portion of it which had been in contact with the bottom of the coagulating vessel is pure white, while the opposite portion is milk-white, this being readily explained by a portion of the powder having subsided in the fluid while at rest. This is, however, of no consequence, the coloration becoming uniform by itself, if in the subsequent rolling of the mass the thin plates are put together, and again rolled.

The other method for combining the pulverulent filling substance with the celluloid, consists in uniformly scattering the powder upon the celluloid plates previously softened, and rolling them repeatedly till the color is uniform throughout.

Celluloid masses combined with a filling substance may also be colored, and articles of very handsome appearance made from them. Special mention may here be made of imitations of genuine coral which, from the most delicate milk-white, or only slightly rose-tinged, kinds up to the deep cinnabar-red varieties, can be produced of such beauty as to be distinguished from the genuine article perhaps only by their higher lustre.

Although filled celluloid masses colored yellowish in a suitable manner closely resemble ivory in appearance, they can at once be distinguished from ivory by the absence of the peculiar texture characteristic of the latter. However,

this texture is also successfully imitated, the resemblance between celluloid imitations and genuine ivory becoming thereby still greater.

For this purpose plates of filled celluloid mass, some of them pure milk-white and others of a color inclined to yellow, are used. These plates are alternately laid one upon the other, heated, and then rolled. By the pressure of the rolls the separate plates are welded together, and by being stretched under the rolls, of course, become constantly thinner, so that the layers of a darker and lighter color are only visible upon the cross-section in the form of fine lines running into each other. If a plate thus rolled, previous to being made into a cane head, button, etc., is bent to and fro, the fine lines are also bent, and such an article has to be very closely examined in order to find out that it is only an excellent imitation of, instead of genuine, ivory.

Tortoise shell can be so closely imitated with celluloid that it can only with certainty be determined by a chemical examination, whether the article in question is made of genuine tortoise shell or is an imitation of it. For the purpose of imitating tortoise shell, a celluloid plate is first colored exactly the ground color of genuine tortoise shell, solution of picric acid to which a suitable quantity of aniline brown has been added being used for the purpose. The peculiar red-brown markings characteristic of tortoise shell are applied by means of a paint-brush with aniline-brown solution to which a small quantity of fuchsin has been added. Such solutions when prepared with very strong alcohol, penetrate deeply into the celluloid mass.

The celluloid plates used for imitations of tortoise shell are highly polished previous to being colored and painted, this being best effected by pressing them against a rapidly revolving cylinder covered with a soft woolen stuff. Since the painted places lose somewhat in lustre, the plates when finished must again be carefully polished.

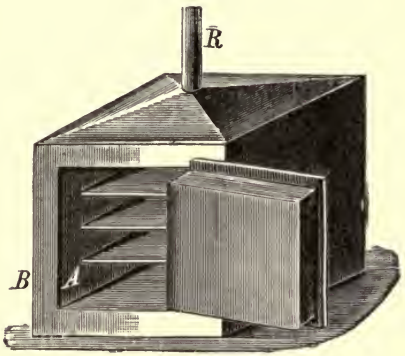
MOULDING CELLULOID ARTICLES.

Pure celluloid, as well as that mixed with filling substances, can in a simple manner be brought into any desired form, it becoming, as previously mentioned, so plastic at 212° F., as to equal, in this respect at least, warmed wax.

When celluloid is to be converted by rolling into plates of any thickness, the simplest plan is to place the thicker plates in hot water until sufficiently softened, and then roll them out as thin as desired.

In case celluloid masses of greater thickness are to be

FIG. 39.



shaped by stamping or pressing, it is advisable to use a special heating apparatus capable of holding a larger quantity of celluloid, so that without interruption in the work, heated pieces may be constantly taken out, and replaced by pieces to be heated. An apparatus very suitable for this purpose is shown in Fig. 39. *A* is a cubical box of stout sheet-iron. It is surrounded by another sheet-iron box *B*, the distance between the walls of the two boxes being 2 to 2⅓ inches. The outside of the box *B*, with the exception of the bottom, is covered with thick felt and the latter with wood. The outside of the thick wooden door of the box *A* is also covered with felt and wood. From the top of the box *B* ascends a pipe *R*, 0.79 to 1.18 inch in diameter. This pipe

terminates in a spiral, open on top, in a cooling vessel filled with cold water. The space between the boxes *A* and *B* is filled with water, and the bottom of *B* is heated by means of a small stove upon which the apparatus stands, or, if the latter is small, by a gas flame. The celluloid masses are placed upon zinc plates fixed one above the other in the box *A*. When the water between the two boxes has been brought to the boiling point, the temperature in the box *A* will in a short time rise to 212° F., and the celluloid masses will, according to their thickness, be in a shorter or longer time heated to the same temperature. The box *A* is only opened for taking out heated celluloid, or for placing pieces to be heated in it.

Since the water by boiling evaporates, it would be necessary from time to time to replenish it. This is, however, rendered superfluous by the cooling arrangement, by means of which the steam rising through the pipe *R* into the spiral portion of the latter in the cooling vessel is condensed, and the hot water falls back into the space between the two boxes. When work for the day is finished and the fire under the apparatus extinguished, the water, by reason of the insulation of the outer box by felt and wood, remains quite hot till the next morning, and but little time is required to bring it to the boiling point.

Celluloid tubes are made as follows: A plate of celluloid is cut rectangularly in such a way that it accurately fits around a cylinder corresponding to the inside diameter of the tube to be made. The cylinder being heated, the softened celluloid plate is laid around it, and a round piece of sheet metal is pushed over the plate so as to hold it in position without entirely covering it. Fluid celluloid is applied to the joint of the plate, and the whole is then left untouched till the celluloid is cold. The finished tube is then drawn from the cylinder.

It may here be mentioned that for the purpose of joining two pieces of celluloid, it has been recommended to soften

them by the application of strong alcohol, and then press them together. Celluloid solution obtained by dissolving nitro-cellulose and camphor in ether is, however, more suitable for the purpose, it solidifying in a very short time, and the two pieces are then joined together by the same mass of which they themselves consist.

If celluloid is to be shaped by pressing, it is advisable, especially when making a large quantity of articles of the same form, to put the lower portion of the mould in the press in such a way that it can constantly be kept, by means of a gas flame, at a temperature which need not be above 158° F. In preparing articles from heated celluloid in a press thus arranged, tearing of the mass on the edges need not be feared, and, with some dexterity, the pressed article can, while still soft and without losing shape, be lifted from the mould, the latter being thus left available for the next operation.

Imitations of corals may be made in various ways, according to the form the separate pieces are to have. Corals of cylindrical shape are cut with a circular saw from sticks made by pressing. Rounded-off (barrel-shaped) corals are stamped from the above-mentioned cylindrical sticks, and pierced in the lathe. The final finish is given to the corals by brightening them by means of rapidly revolving bobs covered with soft cloth.

The use of celluloid masses for the manufacture of all kinds of combs is of great importance. They are made by first rolling a celluloid plate in such a way that one of its narrow sides, which is to form the back of the comb, is thicker than the other. The comb is then stamped from the softened plate. The teeth are cut with a rapidly revolving circular saw kept cool by water dripping upon it, and the finished comb is finally polished.

CLICHÉS FROM CELLULOID.

A very important application of celluloid for the repro-

duction of printed matter consists in its use for clichés which, independent of being non-breakable, are very durable so that thousands of impressions may be made, without their sharpness being in any way diminished. The production of such clichés, either from a form of type or a wood-cut, is a very simple operation, and is effected as follows: A plaster of Paris cast is first made of the form or wood-cut, the best quality of plaster of Paris such as is used for art castings being employed for the purpose. To make the cast harder, saturated solution of alum in water is used, in place of ordinary water, for mixing the plaster of Paris. Such cast requires a longer time for hardening than one prepared in the usual way, but it possesses much greater hardness. When thoroughly dry the cast is saturated with solution of shellac in strong alcohol; with casts from wood-cuts this saturation is effected by applying the shellac solution with a soft brush.

The plaster of Paris mould is then placed in a press and covered with a heated celluloid plate of suitable thickness. The press is then slowly and very uniformly tightened to give the softened celluloid time to penetrate into all the depressions of the mould. The press is finally tightened, and left untouched till the celluloid is cooled to the ordinary temperature. The celluloid plate is then detached from the mould by carefully knocking the latter against a solid support, and the mould, which is not in the least damaged, may be used for making another cliché.

When a celluloid cliché properly made is examined with a magnifying glass, it will be seen that the smallest details have been reproduced, and it need only to be blocked to be ready for printing.

Stamps, the text of which is composed of types may in a similar manner be made from celluloid, such stamps having the advantage over rubber stamps of being more easily made and being more durable.

COLLARS AND CUFFS FROM CELLULOID.

Masses of celluloid and a white filling-substance are well adapted for the manufacture of collars and cuffs which, as regards appearance, can scarcely be distinguished from such articles made of the finest quality of linen, and they have the advantage of greater durability and being more easily cleansed, though the latter can only be done when properly treated.

The white masses for this purpose are prepared from celluloid and zinc-white, or magnesia, or chalk, and rolled out to plates. Pieces of the shape of the collar or cuff are then stamped from these plates.

For the purpose of giving these pieces the appearance of a fine quality of linen, a mould is made as follows: A collar of fine linen is used as a model, and a plaster of Paris cast made of it. From this plaster of Paris cast hollow moulds of type metal are made. The stamped celluloid plates being heated are laid in the moulds, and subjected to pressure by means of a press. The fine threads constituting the tissue of the collar used as a model will be found reproduced true to nature upon the celluloid so that, in appearance, it cannot be distinguished from the linen collar.

Celluloid collars and cuffs, like the genuine linen articles, become dirty by use, and it is claimed they can be cleansed, so as to appear like new, by simply brushing them with soap and water, and rinsing in water. This, however, is not in accordance with the facts, it being impossible in this manner to remove the dirt, and, notwithstanding a vigorous use of the brush, the article does not become perfectly clean. The reason for this is that celluloid mixed with a large quantity (up to 50 per cent.) of filling-substance is by no means an impervious material like pure celluloid; on the contrary, it is quite a porous mass in which the particles of dust settle so firmly that they cannot be removed by brushing with soap and water. The impossibility of thoroughly

cleaning celluloid cuffs and collars may probably be the reason why they have not been more generally introduced.

For the production of celluloid collars and cuffs which can actually be readily cleansed, it would seem necessary to provide the finished article with an impervious coating, pure colorless celluloid being used for this purpose. This coating is prepared by adding, for the purpose of dilution, a certain quantity of absolute alcohol to fluid celluloid—*i. e.*, solution of nitro-cellulose and camphor in ether. The finished articles are for one moment dipped in the solution, whirled around to remove every drop of solution, and hung up free in the air. When the solvent is evaporated, which will be the case in a very short time, the articles will look as having been starched with gloss-starch, their beautiful appearance being due to the thin layer of colorless celluloid with which they have been provided. Such, so to say, lacquered celluloid collars and cuffs may be cleansed in a very simple way by spreading them out smoothly and rubbing with a sponge dipped in lather, drying, and vigorously rubbing with a soft cloth. A brush should not be used, as by rubbing with it the thin layer of celluloid would soon lose its beautiful gloss. By this simple treatment lacquered collars and cuffs can be actually cleansed, and besides are more durable than linen articles which after having been several times washed, are frequently so much the worse for wear as to be useless.

CELLULOID FOR DENTISTS' USE.

In modern times celluloid is more and more employed by dentists, it having gradually supplanted hard rubber, which was formerly in general use for the manufacture of sets of artificial teeth.

The celluloid to be used for this purpose must be of exactly the same color as the gums, and the only dye-stuff suitable for coloring it is cinnabar, on account of its indifference towards the action of the saliva and food. For the

purpose of preparing an intimate mixture of celluloid and cinnabar, the latter has to be reduced to an impalpable powder by levigation. It is best to commence the operation by covering a thin, softened plate of celluloid with cinnabar powder, placing another also very thin celluloid plate upon it, and joining the two plates by rolling, the cinnabar becoming thereby fixed. The plate thus obtained is folded together, heated and again rolled, this operation being repeated till the celluloid is uniformly colored throughout. The work of preparing in this manner a uniform mass being quite troublesome, it would seem advisable to prepare at one operation a larger quantity of such celluloid, and make it finally into plates of the thickness suitable for the use of dentists.

An exact impression of the gums and jaw as required for making a set of artificial teeth is made, as is well known, with plaster of Paris, and the negative thus obtained is made use of for preparing the plates. In making these plates from rubber, an impression in soft rubber is made from the plaster of Paris negative, and heated in the vulcanizing apparatus till it is converted into hard rubber. In working with celluloid, the preparatory operations are the same as with rubber. The celluloid which is to be used for the plates is heated till it is very plastic, and then firmly pressed upon the plaster of Paris cast, remaining thus under pressure till the whole is cooled down to the ordinary temperature.

The temperature to which the celluloid, to be used for plates, has to be heated, is given by dentists as 282° F. However, this is probably too high, celluloid at this degree of heat approaching the point at which it is decomposed. In our opinion, a temperature of 266° to 275° F. is amply sufficient to make the celluloid so plastic as not to require even especially high pressure to force it into the finest depressions of the mould. Care must, however, be taken to heat the celluloid throughout to the above-mentioned degree before pressing is commenced.

OBJECTS OF ART FROM CELLULOID.

By reason of its great plasticity, when heated, celluloid may to advantage be used for the manufacture of all kinds of inlaid work, and with it as a basis-material, beautiful mosaics can be produced, as well as fancy articles inlaid with metal, the latter being generally made of celluloid masses representing an imitation of ivory or tortoise shell.

The metals used for these *incrustations* are gold and silver for valuable articles, and bronze, copper, and aluminium for cheaper goods. The metals are used in the form of very thin sheets, from which are cut by means of suitable dies, stars, bands, leaves, ornaments, monograms, etc.

These small particles of metal are attached to the celluloid by moistening them with strong alcohol, or still better with fluid celluloid, and placing them in their proper positions for the execution of a fixed design.

When the entire design has thus been produced, the celluloid plate is placed upon a firm, level support, for instance a piece of thick zinc-sheet, and uniformly heated together with the latter to 257° F. The plate together with the support is then drawn through rolls, a very slight pressure being first given for the purpose of pressing the particles of metal into the soft celluloid mass. In passing the plate for the second time through the rolls a somewhat greater pressure is given, and the latter is finally increased to such an extent that on touching the plate with the fingers no elevation is noticed, this being proof of all the metallic particles having been sunk into the plate. The latter, when cold, is lightly ground and then highly polished. When such encrusted plates have to be bent, as is necessary, for instance, in the manufacture of cigar cases or pocket books, a metallic negative form has to be used. The celluloid plate is laid upon this form and sufficiently heated to allow of it being readily bent over it.

CELLULOID MOSAICS.

An entirely original application of celluloid masses is their use for the production of mosaics equal in appearance to those of polished stones (*pietra dura mosaics*) chiefly made in Florence.

Celluloid, as previously mentioned, may be colored any shade, and by filling it with colored powders, masses of any desired color may be produced. By coloring celluloid, for instance, blue with ultra-marine and pressing small laminae of mica into the colored mass, a body is obtained which bears a close resemblance to the valuable mineral known as *lapis lazuli*. By partly coloring white celluloid, imitations very true to nature of variegated marble may be obtained, etc.

Celluloid plates thus colored may be used for the execution of works of art closely resembling genuine Florentine mosaics, but, of course, costing much less to produce. Such mosaics are produced by cutting out by means of dies from the basis-plate of celluloid the portions which are to be filled in by differently-colored masses. With the same dies portions are then cut from colored celluloid plates, these portions, of course, fitting exactly into the empty spaces of the basis-plate. To prevent the celluloid plates from cracking while punching out the pieces, they are, previous to the operation, heated to between 122° and 140° F.

In executing the design a painted picture is followed, the celluloid pieces which have been cut from colored plates being placed in the proper empty spaces of the basis-plate, the latter resting upon a level zinc-plate. When the design has been executed, it is heated together with the support, till the celluloid becomes soft, and is then passed through rolls, by the pressure of which the firm union of all the celluloid pieces to a whole is effected. The final finish is given to the plate by grinding and polishing. Before polishing, the color effects of certain parts, where it appears

necessary, may be heightened by carefully painting them with tar colors dissolved in alcohol.

As previously mentioned, such mosaic designs closely resemble in appearance those made of differently-colored stones, but of course are much cheaper.

CELLULOID LACQUER.

A solution of nitro-cellulose and camphor in ether forms the substance which has in this work been repeatedly designated as celluloid solution, and to convert it into solid celluloid nothing has to be done but to allow the solvent to evaporate. If a solution of celluloid be poured upon a level glass plate in such a way that the thick fluid spreads in a thin layer over the glass plate, a thin plate of celluloid is obtained after the evaporation of the solvent, which may be used as so-called films for photographic purposes.

By mixing celluloid solution with a suitable quantity of strong alcohol, a fluid is obtained which dries more slowly upon the glass plate than the solution containing only ether, but leaves behind an exceedingly thin, though perfectly homogeneous, film of celluloid. By dipping an article in this solution, or applying it with a brush, and allowing it to dry, an exceedingly thin coating of celluloid is formed, covering the entire surface of the article and protecting it from the effects of dust and moisture, thus possessing all the properties which may be demanded from an excellent quality of lacquer.

No matter how thin such coatings of celluloid may be, they are perfectly water-proof, and even the most delicate articles may be cleansed with a sponge and soap. The coating may be so thin as not to be noticeable, and if somewhat thicker, imparts to the articles the beautiful lustre characteristic of celluloid. Thin coatings are especially of value for the protection of maps, copper and steel engravings, as well as drawings in general. By coating both the face and back, of a map, water-color painting, or printed

sheet, with dilute celluloid solution and allowing the coat to dry, the paper is rendered almost indifferent to moisture. In case it has become dirty by frequent handling, it can without fear be cleansed by spreading it out upon a support and washing with a sponge and soap water, all the dirt adhering to the celluloid being thus removed without the underlying paper becoming even moist.

A very thin layer of celluloid affords an excellent protection for metals against rust, turning black and, in fact, against all external influences. Collections of armor, weapons, etc., have to be constantly watched to prevent rusting. However, when once made bright and then provided with a scarcely perceptible layer of celluloid, they retain their polish and need only from time to time be freed from dust by wiping with a woolen cloth, to be kept in perfect condition. Even if such articles are kept in a damp room, they show no trace of rust, the iron under the air-tight coating of celluloid being excluded from the action of moist air.

The above-mentioned excellent properties of thin coatings of celluloid have led to the extensive use of celluloid solutions as lacquers. Numerous receipts for the preparation of such lacquers have been published, some of them containing ingredients, the effect of which in the composition is beyond comprehension. A detailed enumeration of such receipts is here out of the question, and only the principles will be given according to which celluloid lacquers for various purposes have to be prepared, the main point being whether a lacquer yielding a strong, tenacious coating is to be made, or one possessing a certain degree of flexibility and elasticity.

The basis-material of all celluloid lacquers brought into commerce under various names, such as kristaline, zapon, victoria lacquer, etc., is nitro-cellulose of a composition representing the soluble form. For the preparation of the various kinds of nitro-cellulose, the reader is referred to the detailed description given in a previous chapter.

An excellent celluloid lacquer may be prepared by simply dissolving nitro-cellulose and camphor in ether. However, by reason of the rapid evaporation of the ether, such a solution, when applied in thin layers, dries almost instantly, especially on a warm day, which is frequently inconvenient. It is, however, quite suitable for lacquering smaller articles by dipping, whirling off the excess of fluid, and swinging the articles for a few seconds to and fro, whereby they become perfectly dry, but it is not adapted for larger articles, as it dries almost under the brush.

Celluloid lacquers are, therefore, best prepared with the use of a less volatile fluid, and, besides ether, quite a number of solvents for nitro-cellulose, such as alcohol, acetone, potato fusel oil (amyl alcohol), benzine, etc., may be used for the purpose.

The best results, as has been found, are obtained by using for the preparation of the solution a mixture of equal parts of pure ether and strong rectified alcohol, and by the process given below a lacquer is obtained which, as compared with other similar products, excels in clearness and lustre.

The perfectly dry nitro-cellulose is weighed and brought together with the corresponding quantity of camphor—2 parts by weight of nitro-cellulose to 1 part by weight of camphor—into a wide-necked bottle, which can be closed air-tight with a well-fitting cork coated with paraffine. The lower end of the cork is furnished with a small hook for the suspension of a small bag of very close fine linen and made in the form of a sausage, which is filled with the nitro-cellulose.

The camphor having been brought into the bottle, the mixture of equal parts of ether and alcohol is poured over it, and the bottle is frequently shaken till all the camphor is dissolved. The bag containing the nitro-cellulose is then suspended to the hook, the bottle closed air-tight with the cork, and placed where it is protected from shocks. The

nitro-cellulose at first swells up very much, and then gradually dissolves in the fluid, the linen bag acting as a filter, and retaining the portion of the nitro-cellulose which only swells up without dissolving. A perfectly clear solution is thus after some time obtained.

The solution thus prepared is, as a rule, too thickly-fluid for direct use as a lacquer, but being miscible in every proportion with alcohol, a lacquer of any desired consistency can be readily obtained.

When applied to an article, celluloid lacquer prepared according to the above-described process, yields a perfectly colorless coating. It may, however, be given any desired color by mixing the clear solution with a tar-color soluble in alcohol. A saturated solution of the coloring matter in alcohol is first prepared and filtered, and a sufficient quantity of it is added to the colorless lacquer to give it the desired shade of color.

Very beautiful effects may be produced with colored celluloid lacquers especially upon paper and bright metals, and they can to advantage be used for lacquering fancy paper and small metal articles. Artificial flowers of paper when dipped in colored celluloid lacquer exhibit, after drying, a very beautiful lustre and do not become unsightly by dust, the latter adhering only loosely to the smooth coating and may be readily blown off. Such flowers may even be cleansed by sprinkling them by means of an atomizer with water until the pure color reappears.

An important application of celluloid lacquers is for the conservation of metals. As previously mentioned, collections of armor and weapons can in the simplest manner be protected from rust by a coating of celluloid, and metallic articles of every description may in the same manner be preserved, so that rusting becomes impossible, and for the purpose of cleansing they need only be wiped with a soft cloth.

A coating of celluloid is said to be of special importance

for metallic articles which come in contact with sea water. By reason of its content of salt, sea water acts very energetically upon metals, and constant cleaning and oiling are required to protect them from becoming rusty, but metal articles coated with celluloid lacquer remained bright when brought repeatedly in contact with sea water. The portions of iron vessels exposed to the action of sea water are, as is well known, strongly attacked, and it has been proposed to protect them by a coat of celluloid. While such a coat would, without doubt produce a favorable effect, a single application of thin celluloid lacquer would scarcely suffice. The use of a thickly-fluid lacquer would be required, and several coats of it would have to be applied in order to fix upon the iron a layer of celluloid about 0.039 inch thick, such a layer being of sufficient thickness not to be worn off, even after a long time, by the friction of the water. Special experiments in this direction are said to have been attended by excellent results, and it is claimed that no barnacles adhere to the smooth surface of the celluloid, as is otherwise the case.

CELLULOID-LIKE MASSES WITHOUT AN ADDITION OF CAMPHOR.

The pronounced odor of camphor of many articles prepared from celluloid is in many cases objectionable, and efforts have been made to substitute for the camphor other substances which, together with nitro-cellulose, would yield a product equal in physical properties to celluloid.

To judge from the large number of substances proposed for this purpose, it may be supposed that either all of them yield with nitro-cellulose substances whose properties correspond with those of celluloid, or, what is more probable, that more favorable results are obtained with some of them than with others.

According to a statement of the *Société générale pour la Fabrication des matiéres plastiques*, the camphor in the manufacture of celluloid may be entirely replaced by naphtha-

line. However, the odor of naphthaline being still more intense and offensive to most people than camphor, the product obtained presents no other advantage over celluloid than that of being cheaper.

Zuhl and Eisemann replace the camphor partly or entirely by a series of various bodies. They enumerate in their patent as suitable for this purpose: α and β naphthyl acetate, phenoxyl or naphthoxyl acetic acids, their anhydrides or esters, methylnaphthylketone, dinaphthylketone, methyloxynaphthylketone or dioxydinaphthylketone, and the esters of the oxanyl acids. By working up 25 kilogrammes (55 lbs.) of oxanyl acid methyl ester either by itself, or together with a solvent, and 75 kilogrammes (165 lbs.) of nitro-cellulose, a suitable product is obtained, as well as with the use of 30 kilogrammes (66 lbs.) of oxanyl acid, benzyl ester and 100 kilogrammes (220 lbs.) of nitrocellulose. In place of camphor, according to the above mentioned authors, may also be used: triphenyl phosphate, tricresyl phosphate or trinaphthyl phosphate, or finally the monohalogen products of substitution of the aromatic hydrocarbons, so that camphor may be entirely banished from the manufacture of celluloid.

J. R. Goldsmith uses in place of camphor, or as a partial substitute for it, acetodichlorhydrin, diacetochlorhydrin and monoacetomonochlorhydrin.

According to a communication of the *Farbwerke*, formerly Meister, Lucius and Brünig, the camphor in the manufacture of celluloid may be, either entirely or partly, replaced by aromatic sulpho-acids derivatives, derived from chlorides, esters and amides. Celluloid-like masses without camphor may be prepared with the use of neutral phtalic acid alkyl ester and phtalic acid alphyl ester. The following example may here be given: Dissolve 1000 parts of phtalic acid diphenyl ester in alcohol and add to the solution 2000 parts of nitro-cellulose. When the nitro-cellulose is completely swelled up, the mass is further worked in the usual way.

The corresponding cresyl ester of the above-mentioned bodies may in the same manner be used.

The *Deutsche Celluloid Fabrik* at Leipzig-Plagwitz replaces camphor in the manufacture of celluloid by acetyl derivatives of secondary aromatic amines.

No matter what substitute may be used for camphor in the manufacture of celluloid, practical success can be achieved only with a substance which yields a product, that, as regards transparency, elasticity and plasticity when heated, as well as capacity of being colored, corresponds with camphor-celluloid, and is entirely or nearly colorless, and can be produced at the same cost.

XIII.

RUBBER COMPOUNDS.

By rubber compounds are understood masses consisting partly of rubber with the addition of other substances, these additions being generally made for the purpose of producing a cheaper article, though in some cases also to impart to the rubber properties otherwise not possessed by it. From rubber alone, for instance, masses with properties like those of whalebone, especially as regards tenacity and elasticity, could not be produced, but it can be done with the use of suitable additions.

The principal substances used as additions to rubber are resins—especially shellac—antimony pentasulphide or gold sulphur, and coal tar pitch. As indifferent filling substances, any powdered materials insoluble in water may be used, for instance, chalc, ferric oxide (colcothar or rouge) or calcined magnesia. The use of the latter may be especially recommended, because with great bulk, it has a comparatively slight specific gravity, and articles filled with it are not conspicuous by great weight.

Of the resins, shellac is most frequently used, it being harder and less brittle than other varieties, and for our purposes the dark-red article known in commerce as ruby shellac is most suitable.

Of the pitch-like substances, large quantities of the best grades of asphalt, as well as coal-tar pitch, are used as additions to rubber compounds. Asphalt combines readily with rubber, but has the disadvantage of a quite low melting point, so that compounds containing a certain quantity

of it, become soft at a comparatively low temperature and generally lose the greater portion of their elasticity.

Coal-tar pitch, large quantities of which are at present produced, is distinguished by having a much higher melting point than asphalt, and besides yields compounds of considerably greater hardness, so that for this reason alone it is to be preferred. Coal-tar pitch is prepared by heating coal tar in a still until the greater portion of the volatile bodies is distilled over, and in the still remains a residue which, on cooling, congeals to a solid mass of a deep-black color. The last products of distillation escaping from the coal-tar pitch only at a temperature of more than 612° F., softening of the compound containing this pitch need not be feared.

Manufacturers engaged in the preparation of rubber masses apply to their products various names, which generally refer to some special property. Thus, masses possessing not much elasticity but a high degree of plasticity, are designated as *plastite*, while others distinguished by great tenacity and flexibility are known as artificial *whalebone* or *balenite*. Masses resembling in their properties and appearance ivory, are called ebonite, etc.

PLASTITE MASSES.

The compounds to which this term has been applied are frequently brought into commerce under the name of hard rubber. This designation is, however, misleading, genuine hard rubber consisting only of a mixture of rubber and sulphur, which has been exposed to a suitably high temperature. It is of a deep black color, quite hard, and nevertheless possesses a considerable degree of elasticity. Plastite masses are also of a deep black color and are distinguished by considerable hardness, but instead of being elastic, are quite brittle.

There are quite a number of receipts for the preparation of plastite masses. In some of them ingredients are given,

the effect of which cannot in any manner be explained, and it may be supposed they have been introduced simply for the purpose of making the receipt appear as something new.

A plastite mass possessing excellent properties has, according to Raimund Hoffer, the following composition:

Rubber	100 parts by weight.
Sulphur	20 to 25 parts by weight.
Magnesia	40 to 50 parts by weight.
Pentasulphide of antimony	40 to 50 parts by weight.
Coal-tar pitch	50 to 60 parts by weight.

The masses are prepared as follows: The rubber is worked by itself in the kneading machine till sufficiently soft, when the finely pulverized ingredients are added, and the whole is worked by mechanical means till a uniform mass results. The latter is then pressed under high pressure in iron moulds, and vulcanized in the same manner as hard rubber. The plastite thus obtained is of a deep black color, possesses considerable hardness, and takes a high polish. It is at present quite extensively used in the industries, since a large number of articles which were formerly made by hand from wood, metal, horn, etc., can be manufactured from it in a more simple, and therefore cheaper, way.

ELASTIC RUBBER MASSES.

With reference to their properties, elastic rubber masses are a medium between rubber vulcanized in the ordinary way and hard rubber, and by a suitable change in their quantitative compositions, they may be made either harder or more elastic.

The chief requisites of masses of this kind are elasticity and tenacity equal to whalebone, and products are now prepared which, as regards these properties, answer all demands, and for many purposes have supplanted the genuine article.

A mass serving for the manufacture of *balenite* is composed of the following ingredients:

Rubber	100 parts by weight.
Ruby shellac	20 parts by weight.
Calcined magnesia	20 parts by weight.
Sulphur	25 parts by weight.
Pentasulphide of antimony	20 parts by weight.

The ingredients are mixed in the same manner as given for plastite. However, the degree of elasticity and tenacity depends to a great extent on the temperature at which vulcanizing is effected; the lower the temperature the more elastic the finished mass will be, and the higher the temperature the more closely the product, as regards its properties, will approach hard rubber.

Balenite finds extensive application in the industries. It is, for instance, much used as a substitute for whalebone in the manufacture of corsets, it being even superior to the latter as regards flexibility. Suitably-shaped plates of it are used for arm and leg splints in surgery, and the bobbins for cotton spinning are now largely made of it. On account of its light weight and indestructibility, it may be highly recommended for the manufacture of gunstocks.

RUBBER-LEATHER.

A product brought into commerce under this name, though possessing excellent qualities, has found but little application in the industries. As indicated by its name, it is claimed to have the properties of leather. However, as regards tenacity and durability, rubber-leather, like all such artificial products, cannot bear comparison with actual leather, though in quality it surpasses perhaps all preparations of a similar character. As compared with actual leather it is distinguished by great flexibility and impermeability to moisture.

Rubber-leather is prepared as follows: A rubber solution is first prepared, or a thick, mucilaginous and much-swollen

mass by working rubber together with a solvent such as oil of turpentine or benzine. Waste fibres of all kind, such as flax, jute, hemp, etc., are then incorporated with the mass, it being sought to bring into it as many fibrous substances as possible. When the mass has finally acquired such consistency that it cannot be further worked between the rolls, it is stretched out into a long, thin band. This band is several times made into a lump which is again stretched out by rolling. By this repeated rolling, the fibres are piled in different directions, forming, so to say, a kind of felt. The mass is finally rolled into thin plates and allowed to lie in the air till the solvent has evaporated.

In the rubber-leather thus obtained, the separate fibres are intimately cemented together by the rubber, and the material is distinguished by great tenacity. As shown by special experiments, a product of still greater tenacity is obtained by impregnating closely woven tissues of not too fine a quality with rubber emulsion, and uniting two or more such tissues by vigorous pressure. The product obtained in this manner, even if quite thin, possesses such tenacity as to be actually suitable for shoe uppers, carriage covers, etc. However, the cost of producing such materials is so high that they are more expensive than genuine leather, and this is very likely the chief reason why they have not been more generally introduced in practice. As mentioned in speaking of the various uses of viscose, tissues may now be made very tenacious and resisting by suitable treatment with thick viscose solutions, they being in every respect equal to tissues impregnated with rubber, but much cheaper.

MARINE GLUE.

This term is applied to a valuable rubber compound, which is of special importance when metallic articles coming alternately in contact with water and air are to be protected from rust.

Marine glue is best prepared as follows: Small pieces of rubber are, by the application of heat, allowed to swell up in a quantity of anhydrous petroleum amounting to twelve times their weight. The mixture having been made uniform by continued stirring and gentle heating, six times the quantity of ruby shellac or asphalt—or in place of the latter coal-tar pitch—is introduced. The mass is then made more thinly-fluid by stronger heating, and stirred till uniform throughout.

For use, the marine glue is carefully melted and heated till thinly-fluid. The temperature required for this purpose being such as to exclude its application by means of bristle brushes, brushes of thin elastic wire are employed.

By adding to the marine glue, while it is being prepared, a few per cent. of sulphur, and heating the articles coated with it to above 392° F., the mass is changed as is the case with all rubber compounds when heated to high temperatures; the rubber is converted into hard rubber. Articles thus treated are actually coated with a thin, but firmly adhering, layer of hard rubber, forming one of the most durable and resisting coats of lacquer known.

XIV.

RUBBER SUBSTITUTES.

It is a well-known fact that the production of rubber does not keep up with its consumption. The constantly increasing demand for it cannot be met, and the price of it goes steadily up, though larger quantities than ever before are now brought into commerce from the Congo districts.

This steadily increasing demand for rubber has also induced the chemist to seek for substances possessing properties resembling those of rubber, but up to the present time none has been found, which equals it as regards elasticity, tenacity, chemical indifference, and insulating power for electricity. However, compounds possessing to a great extent the above-mentioned properties are now successfully produced, and may for many purposes be substituted for rubber. By the invention of such masses great service has been rendered, especially to the electrical industry, because many of them possess the highly-important property of rubber, namely, the power of insulation.

The rubber substitutes may be divided into two groups: Masses containing rubber, but only in subordinate quantity, while the main mass consists of other less valuable substances; and masses which contain no rubber whatever, but are prepared from various substances, and yield a product which may for many purposes replace rubber, thus representing a rubber substitute in the actual sense of the word. According to Steenstrup's method, a material which may be utilized as a substitute for rubber is prepared as follows: Waste rubber is dissolved with the application of heat in drying oils. The resulting solution is strongly heated and,

while constantly stirring, a current of air is conducted through it, till a cooled sample shows the proper consistency.

Since the actual rubber substitutes, *i. e.*, masses containing no rubber whatever, deserve the greatest attention, because no expensive materials have to be used in their production, they being on the contrary prepared from substances, large quantities of which are always at disposal, a more detailed description of them will here be given. They are prepared by a peculiar treatment of oils, and according to their mode of production may be designated: 1. Oxidized oils. 2. Sulphured oils. 3. Oils treated with disulphur dichloride. By treatment with the chemicals, the oils, in all cases, undergo such far-reaching chemical changes that they cannot be called changed oils, but must be designated as products formed from the oils. The general term oil-rubber has been applied to these products, but they may be divided into several subdivisions, namely: *Actual oil-rubber, vulcanized oil, and factis.*

OIL-RUBBER.

Certain oils possess the property of absorbing in the course of time, when exposed to the air, considerable quantities of oxygen, becoming thereby thicker, and are finally converted into quite solid masses, which, however, retain always a certain elasticity. Such oils are called *drying oils*, in contra-distinction to *non-drying oils*, which turn rancid on exposure to air, but remain thinly-fluid. The best known representative of the drying oils is linseed oil, and of the non-drying oils, olive oil.

By raising the temperature the oxidizing action of the oxygen is considerably increased, and with the use of higher temperatures, linseed oil may in a comparatively short time be completely oxidized. This fact, together with the powerful oxidizing action of nitric acid, is extensively made use of in preparing oil-rubber.

The first step in the manufacture of oil-rubber is to bring

the linseed oil into large boilers, preferably heated by gas supplied from a generator-furnace, instead of by an open fire. With the use of generator-gas, the temperature to which the boiler is to be heated can be most accurately regulated, and there is no danger of its contents running over or igniting, which would cause considerable loss.

In the generator-furnace furnishing the gas lies a wrought iron pipe, one end of which is connected with an air-forcing pump, while the other end, close over the bottom of the boiler, terminates in a rose resembling that of a watering pot.

The operation is commenced by heating the linseed oil in the boiler nearly to the temperature at which decomposition commences, but without ever reaching that point. When the linseed oil commences to throw out thick vapors and gets into an undulating motion, resembling that of a boiling fluid, its consistency has already undergone a remarkable change. While before, the oil would run down in a thin stream on a spatula dipped into it, it now shows quite a high degree of viscosity, and runs from the spatula in viscous, thick drops.

When the oil has reached this state, the air-pump is set to work and a current of hot air is uninterruptedly forced through the oil. In contact with the hot air oxidation proceeds very rapidly, and heating for three to five hours is generally sufficient for the conversion of the oil into a viscous mass.

In order to ascertain whether the oil has been sufficiently heated, a sample is taken from the boiler and allowed to cool rapidly upon a metal plate. The drops of oil should at the ordinary temperature congeal to the consistency of hardening glue, and show elasticity when pressed with the point of the finger.

When the sample is of suitable consistency, the oil is brought into iron vats in which it remains till cooled to the ordinary temperature, and is then further worked. The oil

might be allowed to cool in the boiler itself, but this would require too much time, and besides the boiler could not be immediately used for a fresh operation.

The final oxidation of the oil is effected by treating it with nitric acid, the quantity of acid required being the smaller the further the oxidation of the oil in the boiler has been carried. Hence, a fixed proportion of oil to acid cannot be given, and the quantity of the latter required for the contents of the boiler has to be determined by an experiment on a small scale.

The thick oil is brought into large stoneware or porcelain dishes which will bear heating, and the required quantity of nitric acid having been added, the mass is heated, and frequently stirred with a glass rod. By the powerful oxidizing action of the nitric acid, the oil thickens very rapidly and samples have to be repeatedly taken. When a sample cooled to the ordinary temperature appears quite solid and can be readily kneaded with the fingers, the action of the nitric acid is finished. It is of importance to place the dishes in which the thick oil is to be heated with nitric acid in a room which can be thoroughly aired, considerable quantities of nitric oxide being evolved by the action of the nitric acid upon the linseed oil. This gas, as is well known, exerts an injurious effect upon the respiratory organs, and should, therefore, by all means be removed from the workroom.

When reaction is complete, the mass is allowed to cool to the ordinary temperature in the dishes, and is then rolled into thin bands by passing it through two glass rolls very closely set together. The band thus formed is allowed to drop into a large vessel filled with warm water, the greater portion of nitric acid adhering to it being thereby removed. For the purpose of freeing it from the last traces of acid, it is thoroughly worked in a large vessel containing hot soda solution.

The oil-rubber obtained in this manner forms a brown,

elastic mass possessing quite a high degree of elasticity. It is indifferent towards most chemicals, and is not changed by remaining for a long time under water. It dissolves with ease in oil of turpentine, and this behavior may be utilized to increase its elasticity, or to incorporate indifferent substances with it, by adding small quantities of oil of turpentine to the mass while it is being worked in the rolls. In the course of time, oil-rubber loses some of its elasticity, the latter decreasing also to a considerable extent at a lower temperature. Old oil-rubber which has become hard, may however, be restored by cutting it up into small pieces, bringing the latter into a vessel, sprinkling oil of turpentine over them, and closing the vessel air-tight. The mass in a short time swells up in the oil of turpentine, and by kneading can be made into a uniform substance with nearly the same properties as freshly-prepared oil-rubber.

Oil-rubber may for many purposes be used as an excellent substitute for genuine rubber. Thus, for instance, it is very well adapted for cushions for the support of rapidly-revolving machinery to neutralize the shocks to which its parts are exposed. It is, however, especially suitable as an insulating material for electric lines, and, in a softened state, is much used for covering electric wires.

MANUFACTURE ON A LARGE SCALE OF OIL-RUBBER BY MEANS OF THICK OIL.

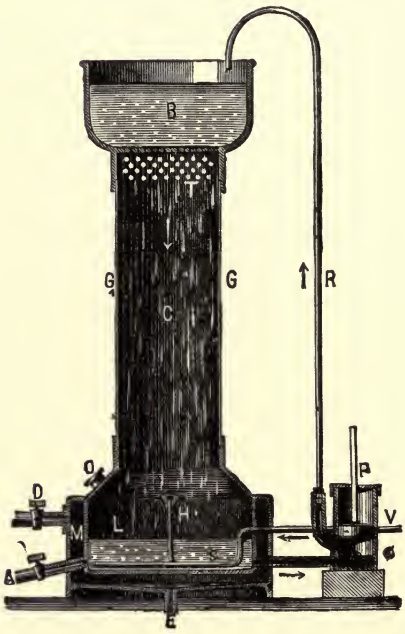
In the manufacture of oil-rubber, as well as in the production of other materials used as rubber substitutes, the linseed oil used for the purpose has by long-continued heating to be highly oxidized till it is converted into a viscous mass. For the purpose of obtaining such a mass, the linseed oil has, however, to be heated for a comparatively long time at a temperature closely approaching that at which decomposition begins.

This operation is, however, not only expensive, but also to a certain extent dangerous—expensive by reason of the

considerable consumption of fuel, and dangerous on account of the ease with which the heated oil ignites, and of the vapors evolved from it, which attack the eyes and respiratory organs.

Since oxidation can evidently take place only where the hot oil is in contact with air, *i. e.*, on the surface, when heating is effected in boilers, oxidation can, of course, be accelerated by giving the oil a very large surface. For

FIG. 40.



the purpose of attaining this object various apparatuses have been constructed, the main feature of which consists in that the oil falls down in the form of a spray, and is met by an ascending current of warm air. Fig. 40 shows an apparatus which answers these demands.

The oil to be worked is poured through the aperture *O* on the boiler-shaped vessel *L*, and *O* is then closed. The

vessel *L* is surrounded by a jacket *M*. The oil is heated by opening the cock *D*, and introducing steam in the space between *L* and *M*, the condensed water running off through *E*. In the vessel *L* lies a pipe rolled into a spiral, which rises free in the centre of the vessel, and is covered by a sheet-iron cap *H*. The end *V* of the spiral pipe projecting from *L* is connected with a ventilator which constantly forces a slow current of air through the pipe *S*. In its passage through this pipe, the air is heated and escapes at *H*. Upon the vessel *L* sits a box several meters high. The sides of this vessel are of glass, so that the oil falling down into the box, is exposed to the action of the warm current of air, as well as to that of light, its oxidation being in a very short time effected by both of these factors. The oil is constantly sucked by a pump from *L*, and forced through the pipe *R* into the reservoir *B*. The latter is furnished with a perforated bottom, so that the oil divided into fine drops falls free through the space *C*, and meets the ascending warm current of air, which escapes from the box *GG* through the apertures at *T*.

As a rule, two to three hours suffice to thicken the oil in this apparatus to the same consistency it would otherwise acquire by long-continued heating to a very high temperature. In addition, this mode of preparing thick oil, has the advantage of the product retaining its light color, while oil thickened by long-continued heating always acquires a dark-brown color.

The thick oil is worked as follows: It is brought into a large stoneware or porcelain dish, and nitric acid diluted with about twice its volume of water having been poured over it, the whole is heated to the boiling point. The linseed oil mass becomes thereby constantly thicker, and finally solid. Boiling is continued until a sample, when cold, scarcely takes the impress of a finger nail.

When this is the case, the mass is taken from the nitric acid and, for the removal of the last traces of the latter, is

repeatedly boiled in water. If the mass is to be brought into any particular shape, it need only be placed in hot water, becoming thereby perfectly plastic and, on cooling, reacquires its original solidity and elasticity.

Oil-rubber may be applied to various purposes, and in many cases serve as a substitute for rubber. Its use for securing large panes of glass in frames might prove of special importance and value. While ordinary putty, in the course of time, becomes hard as stone, oil-rubber always remains elastic, and allows of the expansion of the glass in sudden changes of temperature, cracking of the glass being thus prevented. Oil-rubber being quite tenacious, it might also be suitable for tires for heavy wagons and motor wagons. When softened by heating it may readily be rolled out into thin plates which, when applied by pressure to tissues, adhere firmly to them and render them waterproof.

FACTIS MASSES.

Under the name *factis*, masses have for some time been brought into commerce from England, which may be used as a direct substitute for rubber, as well as an addition to pure rubber, the essential properties of the latter being not perceptibly impaired by the admixture of quite a considerable quantity of them. Factis masses vary very much in appearance, some of them being of a white, or only slightly yellowish, color, while others are more or less dark brown to black. Their consistency is similar to that of quite highly vulcanized rubber.

The result of a chemical examination makes it quite certain that these masses are prepared from a fat oil, and in all of them considerable quantities of sulphur were found, while some of them also contained considerable quantities of chlorine. Based upon these examinations, it was surmised that the factis masses are prepared either from sulphured oils alone, or that they may also be produced by a

reaction of disulphur dichloride upon fat oils. Both these surmises proved correct, and the production of factis equal, as regards properties, to the English article, has been successfully accomplished.

SULPHURED OILS (BROWN AND BLACK FACTIS).

Drying as well as non-drying fat oils, when heated together with sulphur dissolve a considerable quantity of the latter, being thereby converted into viscous masses of a dark color. If the oil, previous to the introduction of the sulphur, be highly oxidized, solid, tenacious, and, up to a certain degree, elastic masses of a dark brown to black color are obtained.

Every kind of fat oil may be used for the production of such masses, though castor oil and rape oil are said to be most suitable for the purpose. The oils may be used in the crude (unrefined) state, the admixed foreign substances, such as mucilage, albumen, etc., being separated during the manipulation.

A weighed quantity of oil is brought into a capacious boiler and quickly heated to about 392° F. The oil rising very much in the boiler, the latter should only be filled at the utmost two-thirds full. By heating, considerable quantities of frothy curd are separated upon the surface of the oil and have to be removed, so that the oil appears as a lustrous, black mass. During the process of heating a current of hot air is forced through the oil till a cooled sample shows a considerable degree of viscosity.

The sulphur to be used should be perfectly free from sulphurous acid. Hence, flowers of sulphur must previously be thoroughly washed and again dried, and roll-sulphur, if used, has to be reduced to a fine powder.

Five parts of oil to 1 part of sulphur are used. An excess of the latter should be avoided, as it would not be dissolved in the mass, but simply distributed in it. The sulphur powder is allowed to run without interruption in a

thin jet into the hot oil, the latter being kept in constant motion by means of a paddle, or what is better, by a mechanical stirrer. Shortly after the introduction of the sulphur, the mass commences to rise very much, and a too vigorous reaction has to be prevented by moderating the fire and by vigorous stirring.

The operation may be considered finished when a sample of the mass dropped upon a cold sheet of metal congeals to a solid body. The contents of the boiler are then brought into shallow, prismatic sheet-iron vessels, and allowed to congeal. The mass, while still warm, is taken from the vessels, and made uniform by rolling. It is finally again softened by the application of heat, and made into blocks by pressure.

This oil-rubber is less often used by itself, but finds considerable application as an addition to rubber for the manufacture of cheaper articles.

Several other substances, chiefly asphalt and vaseline, are frequently added to oil-rubber masses, which are not to be mixed with pure rubber. When vaseline is to be used, it is added to the oil when the latter is heated, and, when melted, intimately mixed with it by stirring. The mixture is then treated with hot air in the above-described manner. If asphalt is to be incorporated with the mass, it is added in small pieces to the hot oil and intimately mixed with it by stirring. A quantity of asphalt equal to 10 per cent. of the oil may be added.

Masses of a dark brown to black color are finally obtained. They may be used by themselves as an insulating material for electrical purposes, though they are chiefly utilized as an addition to rubber.

VULCANIZED OIL.

The product to which this term has been applied is formed by the action of disulphur dichloride upon oils.

If a fat oil, for instance, rape oil, be mixed with a quan-

tity of disulphur dichloride equal to $\frac{1}{10}$ of its volume, the latter at first dissolves without perceptible change. However, a very energetic reaction soon sets in. The mass becomes heated to between 131° and 140° F., evolves vapors of hydrochloric acid, and is converted into a solid transparent substance which, when brought into water, becomes opaque and possesses the consistency of rubber.

While oil-rubber is soluble in oil of turpentine, alkalies, etc., vulcanized oil is distinguished by its great indifference towards the action of chemicals, being not affected even by boiling alkalies and acids.

This indifference may be utilized for the preparation of a varnish possessing great power of resisting the action of chemicals. Dissolve linseed oil in a quantity of carbon disulphide equal to 30 or 40 times its weight, add disulphur dichloride equal to $\frac{1}{10}$ of the weight of linseed oil, and use the mass for coating wood, tissues, metals, etc. The coat becomes dry in a few days, when the article appears as having been coated with vulcanized oil.

WHITE FACTIS.

This product occurs in the form of yellowish-white elastic masses possessing a slight odor of oil. It is not attacked by dilute alkalies and acids. It is produced by the action of disulphur dichloride upon fat oils, and it is a remarkable fact that exactly determined quantities of disulphur dichloride have to be used. If smaller quantities of it are taken the oils are only converted into smeary, gelatinous masses, which never become solid.

R. Henriquez has devoted much time to the investigation of rubber substitutes, and to him we are indebted for the correct method of preparing white factis.

If a fat oil be compounded with a sufficiently large quantity of disulphur dichloride, a mixture of the two fluids is immediately effected. However, the fluid in a short time becomes heated, rises in bubbles, evolves vapors, and is in

a short time converted into a pale-yellow, solid substance, showing scarcely any stickiness or elasticity. The vapors evolved consist chiefly of disulphur dichloride mixed with small quantities of hydrochloric acid and sulphurous acid. By exposure to the air a small quantity of disulphur dichloride evaporates, and the mass then possesses all the properties of the English product.

Dilution of the disulphur dichloride with benzine or carbon disulphide causes the reaction to run its course less violently, but the final product is the same as with the use of pure disulphur dichloride.

Drying, as well as non-drying oils, may be utilized for the production of factis, and, strange to say, the quantities of disulphur dichloride required for the conversion of the different oils into factis vary very much. As shown by comparative experiments, oxidized oils, *i. e.*, oils which have been thickened by blowing hot air through them, require far less disulphur dichloride for the formation of factis than oils not treated in this manner. Oxidized cotton oil yielded a good quality of factis with 20 per cent. of its weight of disulphur dichloride, while 40 per cent. was required for non-oxidized oil. The figures given below for some of the oils most frequently used for the production of factis, as compiled by Henriquez, refer to non-oxidized oils:

100 parts											
					congeal						
Linseed oil . .	with	30	parts	disulphur	dichloride	but	not	with	25	parts.
Poppy oil . . .	"	35	"	"	"	"	"	"	30	"
Rape oil . . .	"	25	"	"	"	"	"	"	20	"
Cotton oil . . .	"	45	"	"	"	"	"	"	40	"
Olive oil . . .	"	25	"	"	"	"	"	"	20	"
Castor oil . . .	"	20	"	"	"	"	"	"	18	"

The manner of preparing factis on a large scale is to some extent indicated by what has been said above. Disulphur dichloride being an expensive article, it would for economical reasons seem advisable to work with oxidized oils, they requiring less of it than non-oxidized oils.

Special vessels of a shape suitable for the purpose should be used for the oxidation of the oil, a shallow pan, upon the bottom of which lies a bent pipe furnished with numerous narrow apertures by means of which hot air is blown through the oil being very suitable. The crude oil having been rapidly heated to between 392° and 464° F., and the scum removed from the surface, a current of hot air is blown through it, whereby the temperature may be increased to about 572° F. When the oil is sufficiently thickened, it is allowed to run in a thin jet into the reservoir, and to cool in it to the ordinary temperature. The preparation of factis is, as a rule, effected in deep boilers enamelled inside, having each a capacity of up to 66 gallons. However, only about 110 lbs. of oil should at one time be worked, since the oil on coming in contact with the disulphur dichloride rises in the boiler, and with larger quantities, reaction would be so violent that running-over of the mass could scarcely be avoided. The boilers should be so arranged in the workroom that over each of them is fixed a hood of boards for catching the vapors, the latter being rapidly removed by means of a powerful ventilator. This precaution is absolutely necessary, as disulphur dichloride is very poisonous and attacks especially the respiratory organs.

The weighed quantity of oil is brought into the boiler and by vigorous stirring set in a rapid rotatory motion, when the required quantity of disulphur dichloride is allowed to run in, stirring being continued so long as the consistency of the mass will permit. The commencement of the reaction is indicated by the appearance of white vapors, and the end of it, by the cessation of the evolution of vapors, when the mass must at the same time have become solid.

The mass is now quickly taken from the boiler and rolled out into thin bands. The latter are placed on nets made of twine stretched in frames, where they remain until the

odor of disulphur dichloride has entirely disappeared. The mass should be entirely odorless, or only show a slight odor of oil. It should not yield soluble bodies of any kind to water. By heating, it must become soft and plastic, and allow of its being rolled or pressed into any desired shape. By themselves, factis masses prepared from oils with disulphur dichloride may be very well used for insulating electric lines, but their principal application is as admixture to genuine rubber, it being thus possible to bring into commerce cheaper rubber articles. The addition of factis is generally effected while working the crude rubber in the kneading machine, the whole being worked until a thoroughly homogeneous mass has been formed, in which the particles of rubber cannot be distinguished from the particles of factis.

SULPHURETTED HYDRO-CELLULOSE AS RUBBER SUBSTITUTE.

A substitute for pure rubber, which may be prepared with the use of sulphuretted hydro-cellulose, discovered by Sthamer, deserves special attention. This compound is obtained by bringing 440 lbs. of finely ground hydro-cellulose into a sufficient quantity of hydrochloric acid of 24° Bé., at the ordinary temperature, so that a thin paste is formed and all is dissolved. To the solution 154 lbs. of disulphur dichloride are added, with vigorous stirring. The fluid after some time becomes turbid and acquires a gray-yellow color. By bringing later on the entire mass into cold water, the sulphuretted hydro-cellulose in the form of a mass, insoluble in water, separates upon the bottom of the vessel. It is brought upon a filter to recover as far as possible the hydrochloric acid, the acid running off first, still showing a strength of 20° Bé. Later on the mass is washed with water until the fluid running off no longer shows an acid reaction.

Pure sulpho-hydrocellulose is very indifferent towards chemicals, and cannot be dissolved in any known solvent.

It appears that the combination may to great advantage be utilized in the rubber industry for the preparation of a very good, and at the same time cheap, substitute for rubber. By heating the sulpho-hydrocellulose together with rubber, it is decomposed, and yields the entire quantity of sulphur contained in it to the rubber, the latter becoming thereby vulcanized. The liberated cellulose at the same time enters into chemical combination with the entire mass, the result being a thoroughly uniform body.

By mixing sulpho-hydrocellulose—about 60 per cent.—with inferior qualities of rubber, and heating, more or less porous masses are obtained, from which tubes and plates suitable for insulating electric lines may be formed. In a moist state, sulpho-hydrocellulose may also be pressed in moulds. The articles thus obtained, when dry, are very hard, of a greasy feel, slight lustre, and should possess the color of wood.

PREPARATION OF DISULPHUR DICHLORIDE.

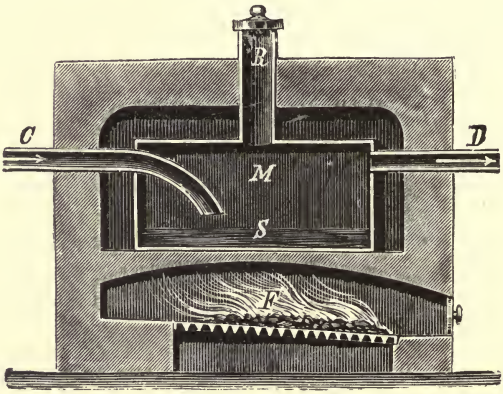
Large quantities of disulphur dichloride are used in the manufacture of vulcanized oil and factis masses, and being rather expensive, it is of advantage to manufacturers of these materials to prepare it themselves.

Disulphur dichloride is obtained by heating sulphur and passing dry chlorine gas over it. The sulphur melts, and the two elements unite to a volatile combination of the composition S_2Cl_2. For the preparation of large quantities of disulphur dichloride, the apparatus shown in Fig. 41 may be used. It consists of the glazed stoneware muffle *M*, placed in the furnace *F*, so as to be uniformly heated on every side. On top of the muffle is a pipe *R*, projecting above the furnace, through which the sulphur to be worked is introduced. During the operation this pipe is closed by a lid luted with clay. The pipe *C*, the end of which is slightly bent downwards, connects with the apparatus for the development of the chlorine gas, and enters the muffle

through the back wall. The pipe *D* placed in the front wall of the muffle terminates in a cooling coil, in which the vapors evolved in the muffle are condensed.

The operation commences with melting the sulphur in the muffle and heating it to between 320° and 338° F., when the chlorine gas is introduced. The latter, before reaching the muffle, must pass through a vessel filled with concentrated sulphuric acid, in order to free it from every trace of moisture. The fire as well as the current of chlorine gas is so regulated that the crude disulphur dichloride runs off in a uniform stream from the cooling coil.

Fig. 41.



The fluid obtained in this manner is by no means a pure product, it containing considerable quantities of sulphur in solution. However, it may be directly used for the preparation of factis, the presence of sulphur in it not having proved detrimental.

For the purpose of obtaining pure disulphur dichloride, such as is required for experiments, the crude product is repeatedly distilled from glass retorts until a distillate boiling at 266° F. and of specific gravity 1.6802, is obtained. The pure disulphur dichloride thus prepared is an oily, red-yellow liquid, fuming strongly in the air, it being, by the

moisture contained in the air, immediately decomposed to sulphur dioxide, sulphurous acid, sulphur and hydrochloric acid. The vessels serving for storing disulphur dichloride must, therefore, be carefully dried and closed air-tight with ground-glass stoppers.

Great care should be exercised in handling disulphur dichloride, the mucous membranes of the eyes, nose and respiratory organs being violently attacked by the vapors of it. The best protection from the vapors for the workman engaged in mixing the disulphur dichloride with the oil, is a head-piece or mask, air from the outside being introduced through a hose connected with an air-pump.

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